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Optimization of an Advanced Water Treatment Plant: Bromate Control and Biofiltration Improvement

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Optimization of an Advanced Water Treatment Plant:

Bromate Control and Biofiltration Improvement

by

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Dedication

This thesis is dedicated to my mother, Julie Bales, who has encouraged and supported me throughout my academic career as well as the rest of my life. I would not be where I am today without her love and support.

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This thesis would not have been possible without the support, knowledge, and mentoring of Dr. Dawn Lei. I am deeply grateful that I was given the opportunity to work with her on this research. I have learned more about research and water treatment than I would have ever thought possible prior to this experience.

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Abstract

The David L. Tippin Water Treatment Facility (DLTWTF) serving the city of Tampa, Florida is an advanced drinking water treatment facility consisting of coagulation/flocculation, ozonation, granular activated carbon biofiltration, and disinfection by chloramine. New regulations and the recent economic crisis pushed the facility to investigate methods to decrease costs and meet regulatory requirements easier.

The two major issues identified as priorities for investigation were the optimization of the biofiltration system and the use of a novel process to reduce the formation of bromate during ozonation.

Optimization of the biofiltration system is needed to remove more of the assorted particles that cause biofilms, nitrification in the distribution system, and high chloramine demand. Previous work improved the removal of particles that cause biofilms and nitrification, but was not able address the removal of particles that cause high chloramine demand to a satisfactory degree. Possible factors affecting this high chloramine decay were identified and evaluated at the pilot scale, including filter depth, chloramination of filter backwash water, media material, and nutrient addition. Non-chlorinated backwash water reduced chloramine demand by approximately 30% for GAC filters, and by approximately 50% for anthracite. Generally, anthracite performed slightly

worse than GAC. Nutrient addition showed no effect. Filter depth improved chloramine decay, but not significantly enough to warrant the increased material required

Bromate control is necessary to prevent the formation of bromate, a regulated carcinogen. Traditional bromate control methods use pH depression. While effective, at the DLTWTF, this forces the increased use of more expensive caustic soda over lime for raising the pH of process water. A novel process known as the chlorine-ammonia process was investigated at the bench scale to identify the ideal ratio of chlorine and ammonia to decrease the formation of bromate to ensure regulatory compliance and allow greater use of lime to decrease costs. The best ratio in this study is 0.45 mg/L NH_3 to 0.75 mg/L Cl_2 which produced 1.09 ppb bromate at a CT of 6.8 min·mg/L, representing a 84% improvement over the control.

Chapter 1: Introduction

1.1: Brief History of U.S. Drinking Water Regulatory Policy

Water treatment in the United States began in earnest in the early 20th century with the application of slow sand filtration, disinfection by chlorination, and lime softening. Over time these methods of treatment were implemented in cities across the country. In the post WWII period, the U.S. Public Health Service was formed and began publishing guidelines for public drinking water utilities, leading to significantly reduced rates of waterborne illness (Craun et al. 2006). In 1970, the Environmental Protection Agency (EPA) was created and tasked with protecting the public health of citizens and the environment (Crittenden et al. 2005). Soon after the creation of the EPA, the Clean Water Act of 1972 was promulgated (33 U.S.C. 1251 1972). While the Clean Water Act did not directly regulate drinking water treatment, it had a significant impact on the water quality of surface water used as the source water by drinking water treatment facilities since the Act specified what could be discharged into navigable waters, resulting in the reduction of all sorts of industrial and domestic pollution streams.

In 1974, the U.S. Congress promulgated the Safe Drinking Water Act (SDWA) regulating most of the public drinking water facilities and source waters in the nation. This law also required the EPA to develop the National Interim Primary Drinking Water Regulation (NIPDWR) and later the National Primary Drinking Water Regulation (NPDWR). These regulations identify specific substances or organisms to be regulated and effective

methods for reducing regulated contaminants (42 U.S.C. 300f 1974). The initial interim NIPDWRs were developed and promulgated in 1976, covering monitoring requirements for 10 inorganic chemicals, 10 organic chemicals, microbial contaminants and radionuclides. The first non-interim set of NPDWRs was promulgated in 1979 and regulated total trihalomethanes (TTHMs). Trihalomethanes are disinfection byproducts created during the chlorination of water containing natural organic matter (NOM). TTHMs include chloroform, bromoform, bromodichloromethane, and dibromochloromethane (EPA 2001). The regulation of Trihalomethanes led to increased interest in alternative disinfection methods. The use of chloramine (free chlorine mixed with ammonia) in lieu of free chlorine was identified as an inexpensive option for the reduction of TTHMs (Brodtmann and Russo, 1979). The EPA proposed the required use of granular activated carbon (GAC) filtration for the control of TTHMs, but industry questioned the efficacy and cost, and were reluctant to invest in a new technology (Pendygraft et. al, 1979). This discussion prompted many utilities to investigate using GAC filtration which resulted in implementation of GAC filtration by some utilities (Cotruvo, 1981). At this time ozone was also identified as an alternative primary disinfectant to replace chlorine with the benefit of less TTHMs production. Chlorine is still needed to maintain disinfectant residual (Rice 1979). Ozone as a primary disinfectant can oxidize NOM that would otherwise be susceptible to become a chlorinated byproduct. This oxidation would lower the amount of TTHMs formed during subsequent chlorination. The decrease in TTHM varies based on source water quality and previous treatment steps.

In 1989, the Surface Water Treatment Rule (SWTR) was adopted under the umbrella of the SDWA. The SWTR added new regulations for *Giardia*, turbidity, heterotrophic plate count (HPC) bacteria, *Legionella*, and viruses. Both GAC biofiltration and ozone were recognized by the EPA for their ability to reduce these contaminants, and their use increased in the U.S. (EPA 1989).

In 1998, the EPA's Stage 1 Disinfection and Disinfection Byproducts Rule (Stage 1 DBPR) and Interim Extended Surface Water Treatment Rule (Interim ESWTR) both went into effect under the Safe Drinking Water Act, placing many previously regulated contaminants such TTHMs, *Giardia*, and turbidity under more stringent regulation and placing new contaminants such as bromate, *Cryptosporidium*, and haloacetic acids (HAA_5) under regulation (EPA 1998). The interim ESWTR increased regulation on turbidity and *Giardia* and added *Cryptosporidium* regulations.

For microorganisms, the EPA grants water utilities removal credits for various treatment processes and also requires testing. *Cryptosporidium* required a 2-log and *Giardia* a 3-log removal based on the ESWTR. Filtration, chlorine disinfection, and ozonation both count as credits towards removal. For instance, *Cryptosporidium* and *Giardia* credits for chlorine disinfection and ozone are granted based on contact time (CT). *Cryptosporidium* and *Giardia* credits for filtration vary based on filter performance. For turbidity, the MCL was decreased from 0.5 NTU to 0.3 NTU. Although TTHMs were previously regulated, the new regulations lowered the MCL from 100 ppb to 80 ppb.

Table 1.1 shows the various regulations for chlorine, chloramines, chlorine dioxide, TTHMs, five haloacetic acids, chlorite, and bromate that were promulgated in 1998. With the exception of bromate, all of the other regulated substances listed in Table 1.1 are typically formed during disinfection by chlorination or are present in the chlorinated product that is added to water for disinfection. Disinfection is a balancing act between protecting public health from the threat of microorganisms and protecting public health from carcinogenic byproducts. The "goal" columns shown in this table represent the ideal situation for the protection of public health. The "limit" column represents the limits that are practically feasible and achieve nearly the same public health outcomes as the goal. The disinfectant residual goals are the same as their limit, because they are directly added by the utility. In an ideal world, there would no byproducts in the finished water, however from a practical engineering standpoint, a value must be chosen that protects public health while also being economically and mechanistically feasible while preventing microorganism growth.

Ozonation started to become more popular as a disinfection method in the United States in order to meet higher disinfection requirements as well as contribute to taste and odor control. With its popularity, the number of drinking water utilities using ozonation has increased from 40 in 1991 to at least 264 in 1998 (EPA, 1999). The increasing market penetration of ozone combined with the new EPA regulations on bromate made bromate minimization increasingly important as bromate is a byproduct unique to ozonation. Bromide is frequently found in source waters in the United States. Under ozone treatment, some bromide will be oxidized to bromate via a complex reaction scheme

involving both molecular and radical reaction pathways. In order to effectively use ozone technology, bromate minimization may be required to meet ozone disinfection goals.

Table 1.1: Maximum residual disinfectant level goals (MRDLGs), maximum residual disinfectant level (MRDLs), maximum contaminant level goals (MCLGs) and maximum contaminant levels (MCLs) for Stage 1 Disinfectants and Disinfection Byproducts Rule, adapted from EPA Federal Register: December 16, 1998 (Volume 63, Number 241)

Disinfectant Residual	**MRDLG (mg/L)**	**MRDL (mg/L)**	**Compliance Based On**
Chlorine	4 (as Cl_2)	4.0 (as Cl_2)	Annual Average
Chloramine	4 (as Cl_2)	4.0 (as Cl_2)	Annual Average
Chlorine Dioxide	0.8 (as ClO_2)	0.8 (as ClO_2)	Daily Samples
Disinfection Byproducts	**MCLG (mg/L)**	**MCL (mg/L)**	**Compliance Based On**
Total trihalomethanes (TTHM)[1]	N/A	0.080	Annual Average
- Chloroform	N/A		
- Bromodichloromethane	zero		
- Dibromochloromethane	0.06		
- Bromoform	zero		
Haloacetic acids (five) (HAA5)[2]	N/A	0.060	Annual Average
- Dichloroacetic acid	zero		
- Trichloroacetic acid	0.3		
Chlorite	0.8	1.0	Monthly Average
Bromate	zero	0.010	Annual Average

N/A Not applicable because there are individual MCLGs for TTHMs or HAAs

1 Total Trihalomethanes is the sum of the concentrations of chloroform, bromodichloro-methane, dibromochloromethane, and bromoform.

2 Haloacetic acids (five) is the sum of the concentrations of mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acids.

1.2: Impact of Regulations on the City of Tampa

The David L. Tippin Water Treatment Facility (DLTWTF) provides drinking water in and around the City of Tampa (Florida). It originally employed a coagulation/flocculation followed by sand filtration treatment. This setup led to high turbidity, TTHMs regulatory violations, and taste and odor control issues. Because of the need to meet regulatory

requirements and to also meet consumer demands for improved taste and odor of the final product, the water treatment plant underwent a large renovation between 2000 and 2002. During that time period the plant added Actiflo^{TM} (a high rate clarifying process), ozonation, and biofiltration by granular activated carbon (GAC), (details of the current treatment facility are provided in Chapter 2). The 2000-2002 upgrade addressed the operational issues that led to turbidity, TTHMs, and taste and odor problems. However, the addition of ozone created two major issues, among other minor ones. One issue is increased chloramine demand at the plant and in the distribution system. The second is bromate compliance, which can be an issue for any utility ozonating bromide containing water. Marda et al. (2008) identified biofiltration as the cause of high chloramine decay, and implemented an operational fix but did not reduce the increased chloramine demand itself. Bromate is currently controlled via pH depression, which is an expensive but effective method of maintaining a low bromate concentration.

1.3: Research Objectives

The overall goal of this research was to address the two major issues caused by ozonation at the DLTWTF – increased chlorine demand and bromate formation. The specific research objectives were to:

1. Reduce the chlorine demand in filter effluent of the biofiltration system.
2. Reduce the operation costs of the biofiltration and/or disinfection system.
3. Reduce bromate formation during ozonation through chemical addition.
4. Reduce the operating cost of pH management by increasing ozonation pH without the risk of a bromate violation.

Research objectives 1 and 2 directly related to chlorine demand whereas research objectives 3 and 4 were related to bromate formation. The chlorine demand issue used a pilot plant at the DLTWTF and the bromate issue its performance under different operating conditions was evaluated.

In terms of chlorine demand, two possible causes for non-ideal biofiltration performance were identified. The first is a lack of bioactivity, allowing NOM and other soluble microbial products to pass into the distribution system, increasing chloramine demand and distribution system nitrification. This is a possible scenario as all the biofilters are backwashed with finished water from the clearwells, which have a residual chloramine concentration of about 5 mg/L. A high chloramine concentration may significantly suppress bioactivity in the filter media. The second possible cause is an excess of bioactivity, leading to excessive sloughing of biofilms into the finished water and the same negative effects. Surface water in Florida is high in NOM, which after ozone treatment will be broken down into lower molecular weight NOM that microorganisms can utilize as a source of carbon (a nutrient). Such favorable conditions might cause the filters to become overloaded with biofilm leading to more microbial soluble products in the filter effluent.

Based on these two possible causes, non-chlorinated water for filter backwash and nutrient addition was evaluated, both of which should promote more bioactivity in the filter media. The GAC and anthracite media were compared side by side for all these conditions. Because anthracite doesn't support bioactivity as well when compared to GAC, the difference, if there is any, should be very revealing and provide more evidence

on the possible cause of high chloramine demand that has been observed in the finished water. Different filter depths for GAC media were studied as well. This won't be a feasible solution to the problem at the DLTWTF because the filter is constructed on the first floor of a 3-story building and filter depth can't be altered. However, such a study will further help understand the issue and ultimately lead to a solution for it.

After the installation of ozonation at the DLTWTF, bromate formation became an issue during time periods when there was high bromide present in the source water. As previously described, bromate is formed during the advanced oxidation processes because of its high oxidative potential. Ozonation is the only mechanism for bromate formation in a typical water treatment process. The three factors with the most significant effect on bromate formation are bromide concentration, ozone dose, and pH. The most common control mechanism is pH control, which was implemented at DLTWTF to control bromate. The literature contains many other mechanistic control strategies, that led to the two objectives related to bromate formation. To achieve these objectives, a bench scale ozonation system was designed and built to research the optimal ratio and concentration of ammonia and chlorine for the specific conditions of the DLTWTF (addressed in Chapter 4).

The remainder of this thesis is organized as follows. Chapter 2 describes in detail the current treatment process of the DLTWTF, the unique water quality of the Hillsborough River, and the associated strategies of dealing with such water. Additionally, Chapter 2 describes the history of the treatment plant, and the subsequent evolution of issues facing the plant over time as new technology was implemented. Chapter 3 examines the

biofiltration process from data obtained in the pilot-scale and compares these results to the full-scale process under various operating conditions. Key variables affecting biofiltration performance were identified and a best resolution for the high chlorine demand problem was proposed. Chapter 4 describes the methods and results of the bench scale bromate formation study, identifying the optimal ratio and concentration of ammonia and chlorine required to reduce bromate and the associated cost savings. Chapter 5 provides conclusions to the thesis and recommendations for further research that are applicable for the DLTWTF and to water utilities.

Chapter 2: The Treatment Process at the David L. Tippin Water Treatment Facility

The David L. Tippin Water Treatment Facility (DLTWTF) treats surface water from the Hillsborough River Reservoir in Tampa, Florida. It is permitted for a maximum flow of 120 MGD and serves around 600,000 people in the City of Tampa. Figure 2.1 shows the treatment process which consists of coagulation and flocculation using ferric sulfate, advanced oxidation by ozone, biofiltration, and disinfection by chloramination.

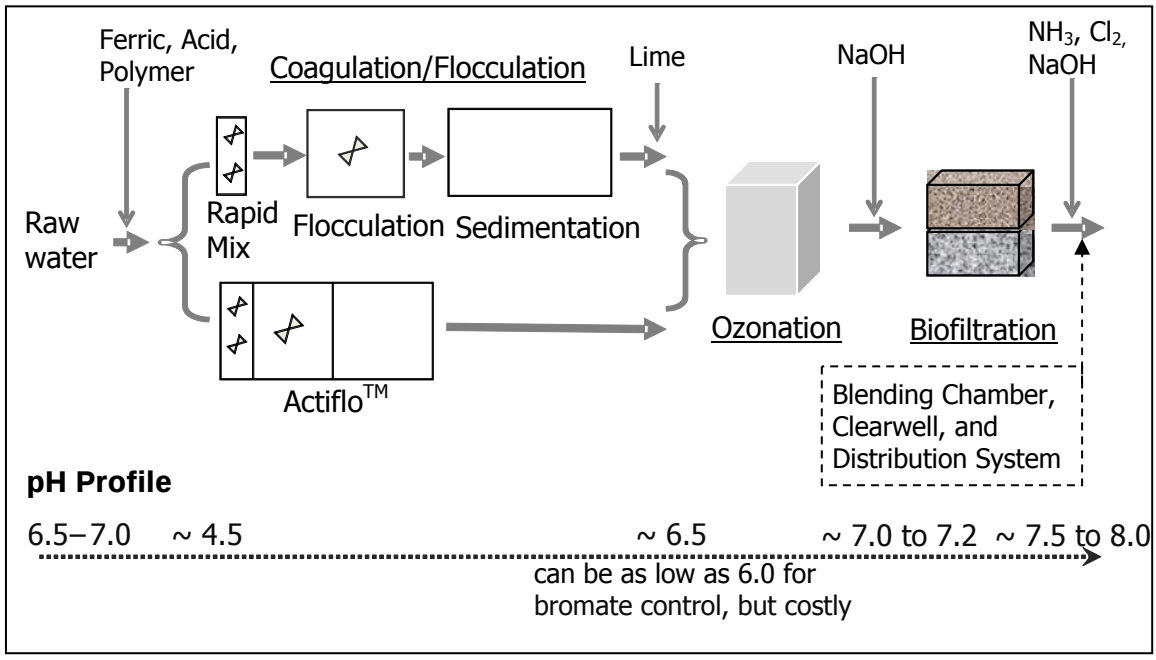


Figure 2.1: The current treatment process at DLTWTF

2.1: The Current Treatment Process

The process begins by pumping water out of the Hillsborough River Reservoir into the parallel rapid mix and Actiflo^{TM} systems. As the water travels between the reservoir and the beginning of the coagulation/flocculation process, sulfuric acid, polymer, and ferric sulfate are added to the water. Actiflo^{TM} is a high settling rate coagulation/flocculation process that uses sand as floc seeds to produce clarified water with a smaller land footprint and less retention time. In the traditional coagulation/flocculation process, ferric sulfate is added creating flocs which attract organic matter in the water. The resulting flocs are provided sufficient residence time to settle by gravity in a sedimentation basin. Clarified water is then collected from the sedimentation basin from the top.

Following these two parallel steps the pH is raised to between 6 and 6.5 by adding lime (calcium hydroxide) before ozonation. Ozonation consists of an eight chambered contactor with weirs located between each chamber controlling flow conditions. Between 0.5 and 3 ppm_m of ozone is diffused into the water in the first two chambers using ceramic discs. The amount of ozone added depends upon water quality and ozone residuals in the 5th chamber of the contactor. Any remaining ozone at the end of the chambers is quenched by the addition of hydrogen peroxide.

Water then travels to the filter junction box, where caustic soda (sodium hydroxide) is used to raise the pH to between 7.2 and 8 for biofiltration. Biofiltration consists of a 24-inch layer of granular activated carbon (GAC) on top of 12 inches of sand. A variety of microbes reside in the GAC and increase the removal of turbidity and low molecular

weight organic material that may contribute to biofilm formation in the distribution system. Manganese oxides and iron oxides are also removed by the filters. Approximately 9 feet of water is maintained above the filter bed and the water filters through at a rate of 1 to 3 gpm/ft^2. Filters are backwashed when they reach an effluent turbidity set point of 0.15 NTU, a run time set point of 96 hours, or headloss set point of 6 feet. During typical operation, the headloss set point is normally reached after 20-50 hours, starting a backwash.

After filtration, water is directed to the blending chamber. Chlorine (dosed from chlorine gas dissolved into a sidestream) is added first, followed by anhydrous ammonia (NH_3) after an approximately 15-minute retention time. Fluoride is added at the same spot as ammonia. Chloraminated finished water is then stored in clearwells until being pumped into the distribution system. Residence time in the clearwell is typically around eight hours.

The water quality of the reservoir that supplies the treatment plant fluctuates largely over the course of the year, impacting the treatment process in many ways. Figure 2.2 shows two of the major water quality indicators, TOC and color, demonstrating the yearly cyclical trend in quality. The source water for the Hillsborough River is primarily the Green Swamp located in Central Florida. During the wet season (June-September), TOC and color both spike due to the large amount of organic matter flushed out of the swamp and tributaries by heavy rains into the river. The relationship of rainfall to TOC and color can be seen Figure 2.2.

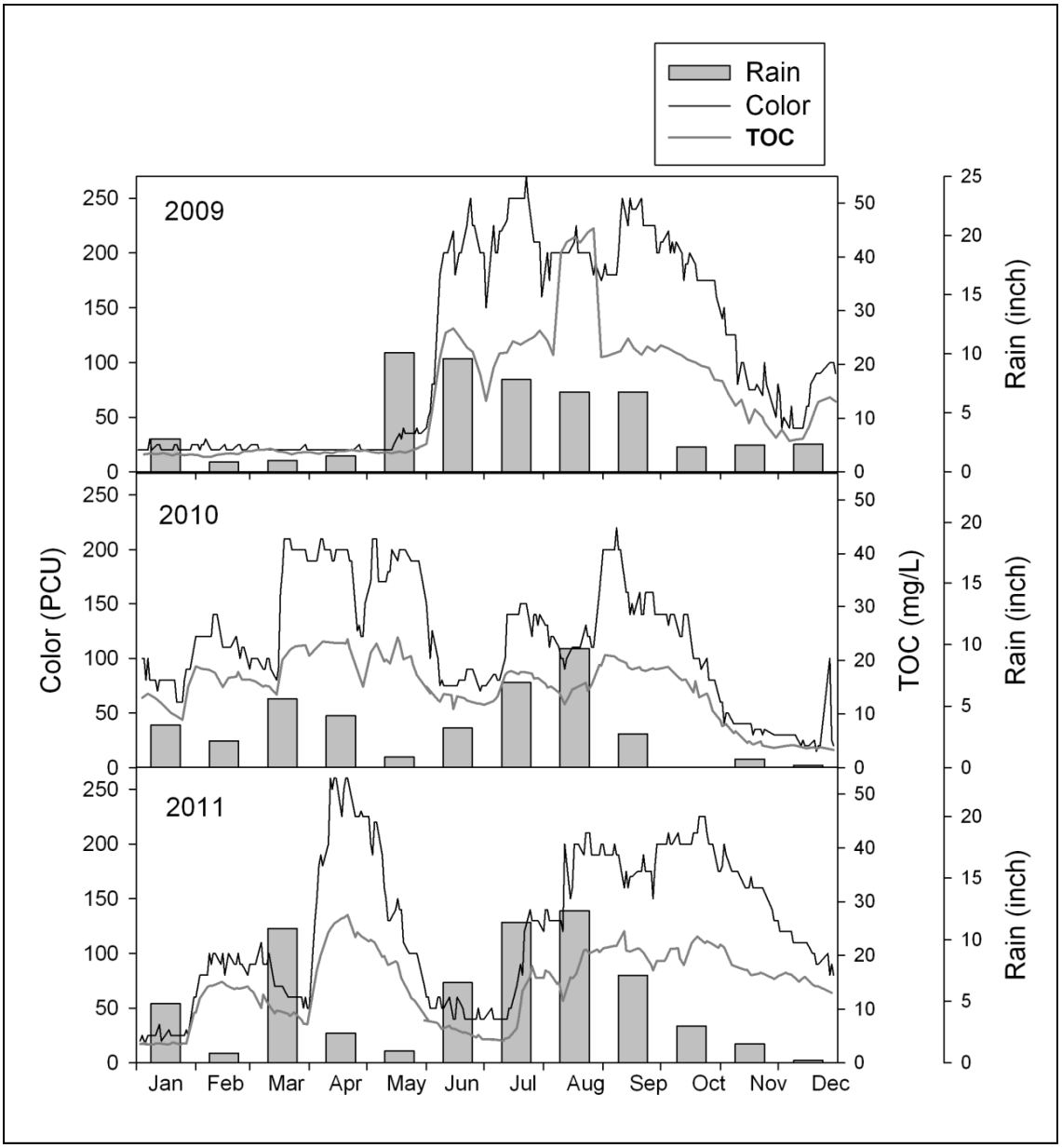


Figure 2.2: Seasonal differences in TOC and color of Hillsborough River raw water, 2009-2011

Table 2.1: Raw and finished water quality metrics at the DLTWTF, September 2010 to June 2011

ANALYTE	UNITS	Raw Water				Finished Water			
		Mar 2011	Jun 2011	Sep 2010	Dec 2010	Mar 2011	Jun 2011	Sep 2010	Dec 2010
ALKALINITY, TOTAL	ppm	121	133	72	148	93	90	65	118
AMMONIA	ppm	<0.1	<0.1	<0.01	<0.01	0.4	0.7	0.5	0.3
ARSENIC	ppm	0.001	0.001	0.001	<0.001	<0.001	<0.001	<0.001	<0.001
BROMATE	ppb	<0.5	<0.5	<0.5	<0.5	1.6	6.5	1.4	4.0
BROMIDE	ppb	68.1	118	76	76.1	89.6	181	45.8	103
B.O.D.	ppm	1.8	1	1	2	2.2	1.8	1.9	1
CALCIUM	ppm	56	64	27	62	74	89	45	78
CHLORIDE	ppm	22.7	27.4	14.2	22.3	43.9	60.3	21.0	42.1
COLOR	PCU	90	60	200	30	<5	<5	5	<5
CL RESIDUAL	ppm	-	-	-	-	4.8	4.7	4.3	4.5
CONDUCTIVITY	MMOHS	398	455	218	490	670	784	407	774
COPPER	ppm	<0.01	0.23	<0.01	<0.01	0.03	0.04	0.02	0.03
DISSOLVED OXYGEN	ppm	5.6	4.2	2.0	6.5	11.4	13.4	11.7	6.8
DISSOLVED SOLIDS, TOTAL	ppm	259	290	170	277	419	486	238	479
FLUORIDE	ppm	0.1	0.2	0.2	0.2	0.5	0.7	0.8	0.8
HARDNESS, TOTAL	ppm	182	200	96	212	220	248	130	270
IRON	ppm	0.12	0.09	0.34	0.08	0.04	0.04	<0.02	0.05
MANGANESE	ppm	0.011	0.010	0.009	0.01	<0.001	<0.001	0.002	<0.001
NITRATE	ppm	<0.025	<0.025	0.048	0.03	0.040	0.093	0.168	0.160
NITRITE	ppm	<0.005	<0.005	<0.005	<0.005	<0.005	0.012	<0.005	<0.005
NONCARBONATE HARDNESS	ppm	61	67	24	64	127	158	65	152
ODOR	TON	17	24	17	17	2	2	1	2
ORGANIC CARBON, TOTAL	ppm	13.1	8.8	20.7	4.5	2.9	1.3	2.8	1.5
ORTHO PHOSPHATE	ppm	0.06	<0.05	0.33	<0.05	<0.05	<0.05	<0.05	<0.05
pH	ppm	7.51	7.87	7.12	7.76	7.56	7.84	7.84	8.12
PHOSPHORUS, TOTAL	ppm	<0.046	0.095	0.3	<0.1	<0.046	<0.046	0.1	<0.1
SODIUM	ppm	12	16	8	8	44	56	22	38
SULFATE	ppm	33.1	45.3	7.1	55.9	167	194	83	197
SUSPENDED SOLIDS, TOTAL	ppm	1	3	6	2	<1	<1	<1	<1
TURBIDITY	NTU	1.7	1.8	1.9	1.7	0.1	0.1	0.1	0.2
UV-254	cm-1	0.491	0.293	0.892	0.145	0.047	0.038	0.047	0.039

Many other water quality characteristics vary seasonally; Table 2.1 shows common water quality metrics for September 2010 through June 2011 for raw and finished water, demonstrating this variance and providing insight into the unique challenges of the Hillsborough River Reservoir water. These large seasonal variations effect the operation of the plant, which is reflected in increased ozone demand and decreased filter performance during the wet season, resulting in higher operational cost. However, the low alkalinity lowers the amount of pH adjusting chemicals, such as caustic soda and sulfuric acid, required.

During the wet season (June-September), extra water is treated and pumped into a series of Aquifer Storage and Recovery (ASR) wells. These wells are 300 to 600 feet deep. ASR water is then pumped back out during the dry season (October-May) to supplement production. Approximately 1 billion gallons are stored and recovered every year. The ASRs allow the DLTWTF to supply all of the water for the City of Tampa during all but the worst droughts, saving the City from purchasing more expensive water from the regional wholesale drinking water utility, Tampa Bay Water. Prior to the installation of ASR system, the Hillsborough River Reservoir was often an insufficient supply during April and May. Water demand also peaks during the driest months as residential and commercial irrigation requirements peak, exacerbating the supply issue. The seasonal rain patterns are displayed in Figure 2.3.

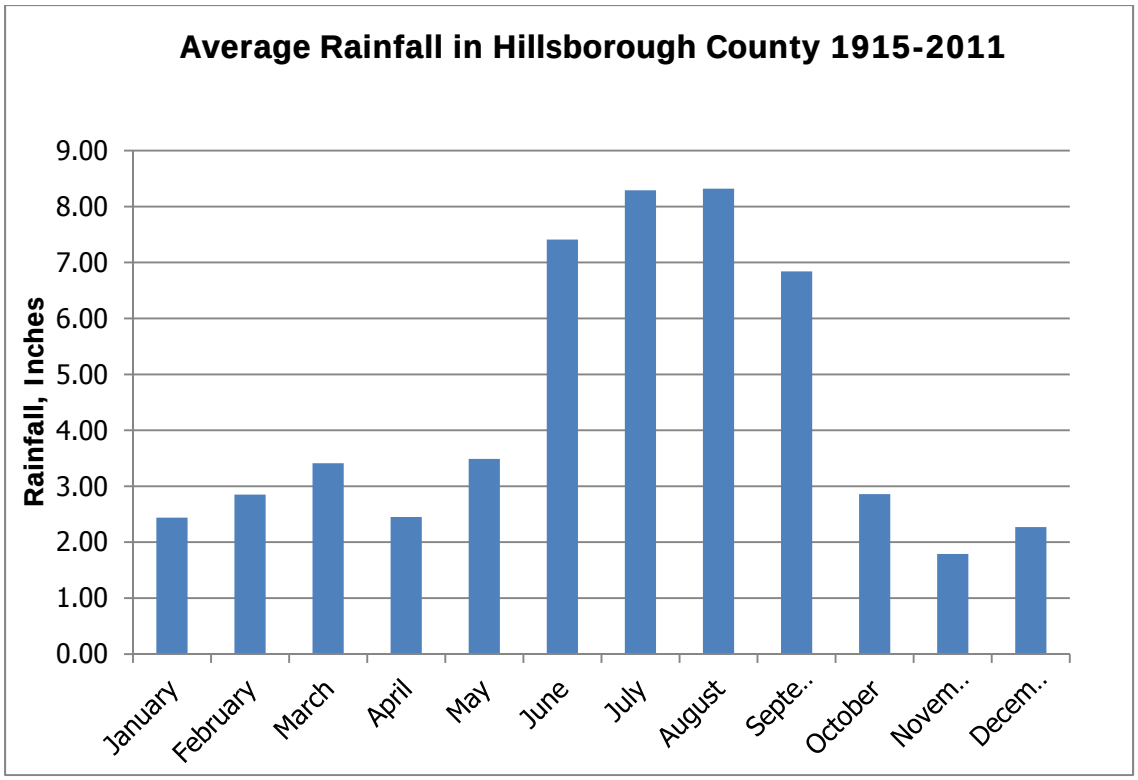


Figure 2.3: Average monthly rainfall in Hillsborough County 1915-2011, data accessed 7/24/2012 from the Southwest Florida Water Management District

2.2: Historical Issues and Remedies

As mentioned in Chapter 1, in the past the DLWTF had used a simpler coagulation/flocculation and sand filtration plant. In 1998, the EPA promulgated both the Stage 1 Disinfection and Disinfection Byproducts Rule (presented earlier in Table 1.1) and the Interim Enhanced Surface Water Treatment Rule (Interim ESWTR) (EPA 2001). One effect of this change was a decrease in the MCL for TTHMs, going from 100 ppb to 80 ppb. The DLTWTF had a typical annual average of around 80 ppb, meaning violations were likely to occur in the future if changes were not made. The Interim ESWTR rule also added new requirements for turbidity, *Giardia*, and *Cryptosporidium*. The DLWTF was not equipped to deal with these new issues without significant changes. These issues led to the complete upgrade and overhaul of the plant to its current state,

adding Actiflo^{TM}, ozone, and biologically activated carbon filtration to increase removal credits for *Giardia* and *Cryptosporidium* while lowering turbidity and TTHM formation. As mentioned before, Actiflo^{TM} does not vary significantly from typical coagulation/flocculation processes, so ozonation and biofiltration were the primary mechanism for the improvement of these four water quality indicators.

The resulting capital project has addressed the taste, odor and TTHMs problem, but also presented new issues. Chloramine started to decay much faster in the distribution system and it became a daily battle for operators to maintain the disinfectant residual, especially at the further points of the distribution system, a problem that was not experienced before the ozonation system was put online. This very same problem was later reported by Wilzack et al. (2003). An increased chloramine and chlorine decay was noted after the water was treated by either ozone alone or ozone followed by GAC biofilters when compared with water treated by GAC biofilters only.

Originally, the plant dosed ammonia immediately followed by chlorine to form chloramine. Prior to installing ozonation, there was not much chlorine demand for finished water and it was quite easy to maintain disinfectant residual in the distribution system. Right after the treatment upgrade, chloramine in the finished water started to experience a rapid decay making it difficult to maintain disinfectant residual in remote sections of the distribution system. Marda et al. (2008) proposed to switch the dosing order of chlorine and ammonia. Previously, both were added at the same time. The proposal had chlorine added first, followed by a 15-minute delay, then ammonia, to allow most chlorine demand to be addressed in the blending chamber prior to entry to

the distribution system. Because chlorine is more reactive than chloramine, this allows significantly more chlorine/chloramine decay to happen prior to entry to the distribution system. This change improved operational ability, but did not directly affect the higher chlorine demand and the associated higher chemical cost problem caused by the implementation of ozonation.

Marda et al. (2008) identified other issues that may have been part of the cause of the high chloramine decay. By performing a chloramine decay study on samples at different times elapsed after a backwash, the study found very high decay immediately after backwash, decreasing over time. This was assumed to be caused by the sloughing of biomass, especially extracellular polymeric substances (EPS), supported by the fact that heterotrophic bacteria plate counts increased during the same time period. The only remedy identified was dosing free chlorine on the top of the filter; however this was only briefly tested and would likely not be feasible in the long term due to increased formation of disinfection by-products and a decrease in the effectiveness of removing other organic matter by microbial action. Further exploring the issue, Marda et al. (2008) found the backwash sequence implemented at DLTWTF was not ideal. Comparing to the procedures at the nearby Tampa Bay Water Regional Surface Water Treatment plant, the air scour time and high-rate backwash time were likely insufficient. This observation was supported by the literature as well (e.g., Ahmad and Amirtharajah 1998, Amirtharajah 1993, Miltner et al. 1995). Accordingly, changing the backwash procedure to include a longer high rate backwash and air scouring time decreased chloramine decay by 50%.

The introduction of ozone to the treatment process caused many of the issues outlined by changing the makeup of the NOM. Typically, filtration (along with the rest of the treatment train preceding it) is very effective at removing NOM. Ozone increases the rate of chlorine decay by breaking up NOM into significantly lower molecular weight organic matter, which is able to pass through filtration and into disinfection. When chlorinated, this NOM causes some chlorine decay as well as producing TTHMs. Any NOM that is not reacted with chlorine continues into the distribution system. NOM in the distribution system increases biological activity by providing an energy source for any microbial activity, leading to biofilms, which are formed as a protective layer around colonies of microorganisms. NOM also forms organic chloramines which diminish the effectiveness of disinfection. In addition, when biofilms form, they provide an environment for ammonia-oxidizing bacteria to thrive, which feed on the ammonia left behind by reacted chloramines (Wilczak et al. 1996, Odell et al. 1996).

The ASR system was installed during the same time period as ozone and biofiltration were added to the treatment process. The high dissolved oxygen content of finished water pumped into the ASR wells frees bromide and arsenic from the geological formation. Dissolved oxygen in finished water from DLTWTF can be as high as 15 mg/L because of the ozone system. Of the gas flow system going into ozone, approximately 93% is oxygen gas and 7% ozone. All ozone that does not react with organics or other substances in the water will also naturally decay to oxygen. When the ASR project was planned, it was thought the water coming out of the ASRs could be sent to the distribution system directly after simple chlorination disinfection, but the arsenic problem forced the recovered ASR water to be sent back to the treatment plant to use the

existing flocculation and coagulation process for arsenic removal. The excessively high dissolved oxygen caused by ozonation was not accounted for during planning, because the ozone system had not been installed yet and previous water quality data was used. With bromide enriched ASR water being treated twice for arsenic removal, bromate formation became an issue. The excess bromide released from the geological formation significantly increases the bromide concentration in the water entering the ozone contactor, increasing bromate formation. Bromide in the natural water is typically between 60 and 150 ppb, which only causes bromate issues when a large ozone dose is used. Bromide concentrations in recovered ASR water are typically in the range of 1200 to 1600 ppb. Thus, the percentage of ASR water fed to the front end of the plant has to be controlled based on this extra bromide to balance the need for ASR supplies with bromate formation.

Bromate control through pH depression is commonly used in drinking water utilities. Due to a lack of other options, the DLTWTF has used this costly method since ozonation and the ASR system was installed. A decreased pH inhibits bromate formation; however, keeping pH depressed prior to ozonation is expensive due to the differences in chemicals used at DLTWTF. After coagulation/flocculation, the pH is already quite low, and lime (calcium hydroxide, $Ca(OH)_2$) is used to raise the pH before ozonation. After ozonation, caustic soda (sodium hydroxide (NaOH)) must be used for any further pH increases, as lime will cause turbidity issues. Lime has a fourfold advantage over caustic soda, as it costs half as much, and its bivalent nature makes it twice as effective. If the pH of ozonation can be raised to 7 without a subsequent increase in bromate formation,

significant costs savings can be realized through the increased use of lime and decreased use of caustic soda.

The plant currently can handle both bromate and high chloramine demand problems without any regulatory violations, but at a significantly higher chemical cost than the ideal case. Bromate control through the chlorine-ammonia process has been shown to be effective in other full scale drinking water treatment plants, meaning the DLTWTF could realize significant savings (Wert et al. 2007). Similarly, to address high chloramine demand issue, more chlorine and ammonia are applied at the plant. These have brought excessive financial stress to DLTWTF's tight budget under the current economic conditions and hence have become important issues to be resolved.

Chapter 3: Pilot Study of Biologically Activated Carbon Filters

3.1: Background

As discussed in Chapter 2, the David L. Tippin Water Treatment Facility (DLTWTF) uses biologically active granular activated carbon (GAC) filtration as the final treatment step prior to disinfection by chloramine and entry into the distribution system. High instantaneous chlorine or chloramine demand requires the addition of larger amounts of chemicals to maintain significant residual level at the farthest point in the distribution system, significantly increasing chemical costs and the production of disinfection byproducts. The David L. Tippin Water Treatment Facility (DLTWTF) added ozonation and biologically activated filtration (BAC) to the conventional treatment process (flocculation/sedimentation/sand filtration) in 2000. Soon after, many issues with monochloramine decay and formation efficiency surfaced. A study conducted by Marda et al. (2008) recommended two solutions to the problem: the backwash procedure was updated to include a longer air scour and high rate backwash, and chlorine addition was placed upstream of ammonia addition. The former solution actually reduces the amount of organic matter that increases chlorine demand, while the latter simply allows for better operational control of a high chlorine demand in the finished water. Since chlorine reacts with biological constituents significantly faster than chloramine, equilibrium can be reached in minutes rather than hours, allowing operators to adjust the chlorine feed accordingly. This brings about a more stable residual disinfectant in the finished water and throughout the distribution system.

Wilczak et al. (2003) found that ozone combined with biofiltration using GAC caused increased chlorine demand. Ozone alone and ozone followed by filtration with new non-biologically active media did not cause as much of an increase in chlorine demand as the combination of biofiltration and ozone. TOC also decreased the most when using both ozone and biofiltration; typically TOC decreases coincide with decreases in chlorine demand, which means something else must be causing chlorine demand. More intensive backwash procedures did not decrease chlorine demand. Based on this evidence, Wilczak et al. (2003) hypothesized that this could be caused by bacterial cells shedding into the filter effluent. Marda et al. (2008) came to a similar conclusion attempting to remedy the situation at DLTWTF. Vokes (2007) found the same issues with ozone and biofiltration causing high chlorine demand.

Biofiltration is commonly installed and operated with ozone because of the reactive effect ozone has on natural organic matter. Ozone breaks down natural organic matter, increasing the percentage of biodegradable organic carbon (BDOC), increasing the percentage of carboxylic acids, increasing assimilable organic carbon (AOC), and decreasing the average molecular weight (Huck et al. 1991, van der Kooij et al. 1982, van der Kooij et al. 1989, Janssens et al. 1985, Westerhoff et al. 1998). With these changes to the NOM, biofiltration is needed to remove this smaller biodegradable to prevent regrowth of biofilms in the distribution system as well as limiting the production of disinfection by products.

Biofiltration prevents regrowth in the distribution system by relying on bioactivity in the filters to consume biodegradable carbon, increasing the biostability of the finished water

in the distribution system. (Escobar et al. 2001, LeChevallier et al. 1992, Rittmann et al. 1989, Urfer et al. 1997, Wang et al. 1995, Bouwer and Crowe 1988, Price et al. 1993). LeChevallier et al. (1991) found AOC to be the limiting nutrient of biofilm formation based on the nutrient molar ratio of 100:10:1 (carbon:nitrogen:phosphorus) required by heterotrophic bacteria. LeChevallier et al. (1996) found a direct correlation between AOC and regrowth potential. If the biodegradable carbon is not removed, it acts as a food source for heterotrophic bacteria in the distribution system. Whichever bacteria thrive create biofilms, providing a safe harbor for all other microorganisms, the most concerning of which are pathogenic bacteria such as *Escheria coli* (Camper et al. 1991, Rice et al. 1991).

The ozonated NOM has been indicted as a primary cause of disinfection byproduct formation (Reckhow et al. 1990, Reckhow and Singer 1990, Rice and Gomez-Taylor 1986). Westerhoff et al. (1998) presented a possible mechanism for the increased formation rates of TTHMs and other DBPs based on the changes that occur in the NOM during ozonation.

Total organic carbon (TOC) and dissolved organic carbon (DOC) are the common water quality parameters used to measure organic carbon in drinking water treatment. If one wishes to relate these two parameters to the biological activity of a water, they become less useful, as large amounts of TOC and DOC are unable to be utilized as a nutrient source for microorganisms. In addition, TOC and DOC cover a variable mix of organic compounds that are not useful metrics in biological processes. Only measuring compounds that can be utilized by microorganisms is important for drinking water

treatment because the primary concern is re-growth of bacteria in the distribution system. The use of carbon bioassays allows for greater resolution in the evaluation of treatment technologies. The two most common methods for measuring the amount of biologically available carbon are biodegradable organic carbon (BDOC) and assimilable organic carbon (AOC). BDOC uses the natural microorganisms present in the water tested and tracks dissolved organic carbon (DOC) until a plateau is reached, and the value of BDOC is the difference between the initial and final concentration of DOC (Servais et al. 1987). AOC uses a fluorescent strain of *Pseudomonas* and measures the carbon that is assimilated into cell mass, which is then converted to a carbon value based on a calibration or conversion factor (van der Kooij et al. 1982). This method was later modified to include a *Spirillum* strain (Huck et al. 1990). BDOC typically represents a larger percentage of TOC than AOC, with concentrations ranging from 10-60% of TOC in natural waters compared to <5% for AOC (Servais et al. 1987). Escobar and Randall (2001) reported that using only one bioassay can lead to under- or over-estimation of the bacterial regrowth potential of the water, as different mixtures of biodegradable carbons can cause one assay to increase more than the other.

An alternative chemical analytical method for measuring carboxylic acids can be used to measure a portion of AOC. Formate, acetate, and oxalate typically account for around half of AOC (Hammes et al. 2006). As a chemical analytical method, it has a much lower turnaround time and typically provides more consistent results compared to bioassays.

As a single cause of increased chlorine/chloramine demand in biofiltration has not been identified, multiple avenues of improving the post-filter chlorine/chloramine demand

have been investigated. Amirtharajah (1993) examined the importance of the air scour process during the backwashing of filters, where air and water are used simultaneously to create a phenomenon known as "collapse-pulsing." A high speed camera was used to confirm the theoretical basis of the method. Collapse-pulsing increases the detachment of particles during backwash, preventing mud-ball formation and increasing filter effluent quality after backwash. Ahmad et al. (1998) found collapse pulse backwashing followed by traditional water backwash with at least 25% bed expansion produced water with lower AOC than without air scour. It also produced lower AOC than a non-biological filter. Ahmad et al. (1998) also found non-chlorinated water to produce water with lower AOC. Miltner et al. (1995) found that non-chlorinated backwash water led to increased removal of aldehydes and AOC compared to chlorinated backwash water. Vokes (2007) found non-chlorinated backwash water led to lower chloramine decay compared to chlorinated backwash water. Wang et al. (1995) found significant improvements in the removal of aldehydes and TOC using non-chlorinated backwash water compared to chlorinated backwash water.

GAC exhibits many advantages over anthracite for biofiltration. Ahmad and Amirtharajah (1998) found that bacteria remain attached to GAC better than to anthracite during backwash. Wang et al. (1995) found that GAC could hold 3 to 8 times more biomass than anthracite. Urfer et al. (1997) found that GAC filters provided better aldehyde removals at colder temperature and established biofilms quicker than anthracite. They also found that anthracite filter performance is negatively affected by chlorinated backwash water significantly more than GAC.

Filter depth appears to have a limited effect on biofiltration compared to traditional filtration. Wang et al. (1995) found that most bioactivity occurred in the top 15 cm of a biofilter, suggesting that most NOM removal occurs near the top of biofilters, making filter depth less important. Velten et al. (2011) found the highest biomass concentration 45 cm from the filter top, which decreased to the bottom of the filter by a factor of 2.3.

Carbon has been found to be the limiting nutrient for biofilm formation in multiple studies on finished water regrowth, and correlated with AOC (LeChevallier et al. 1991, LeChevallier et al. 1992, Chandy and Angles 2001). Chandy and Angles also found that biofilm formation corresponded with increase chloramine decay rates. LeChevallier et al. (1991) identified the molar ratio of 100:10:1 of carbon, nitrogen, and phosphorus, respectfully. Based on this research where biofilm development is being prevented, Lauderdale et al. (2012) investigated the addition of nutrients to biofilters, where biofilm development is a positive trait. They also identified the carbon, nitrogen, and phosphorus in pre-filtration water and added ammonia and phosphorus to the top of filters based on the molar ratio used to predict limiting nutrients. The basis for this is two-fold: For one, if insufficient ammonia and phosphorus are available, bacteria in the filters are not removing the maximum amount of biodegradable carbon possible. Alternatively, bacteria produce more biofilms when "stressed"; a nutrient in limited supply may increase the amount of biofilm material formed in the filters, leading to excessive clogging.

The primary materials of biofilms are extracellular polymeric substances (EPS). Liu et al. (2006) identified the relationships between nutrients and microbial production and

secretion of EPS. Lauderdale et al. (2012) found that nutrient addition decreased terminal head loss by approximately 15%. Barker and Stuckey (1999) review soluble microbial products (SMPs) in the effluent of biological process involved in wastewater treatment, of which EPS is a constituent. SMPs are the assortment of organic products and by products of the microbial reactions involved in biological treatment. While most SMPs research is in wastewater treatment, it is likely that SMPs and EPS have effects that have not been quantified on biological filtration in drinking water treatment.

3.2: Materials and Methods

3.2.1: Experimental Methods

The pilot plant filters used in this study, that emulate the full scale system at the David L. Tippin Water Treatment Facility, take water directly from the filter junction box, where caustic and polymer are added prior to full scale biofiltration. The six rectangular filters are $1ft^2$ and were operated at loading rates of 1-2.5 gpm/ft^2 and height of 9 feet, with turbidity, headloss, and flow rate recorded to supervisory control and data acquisition (SCADA) software. Turbidity was measured by a HACH (Loveland, CO) model SC100 controller with a 1720E sensor verified monthly and calibrated every 3 months. Headloss was measured by an Endress & Houser (Greenwood, IN) model PMD70 calibrated every 6 months. Flow rate was measured by a Endress & Houser (Greenwood, IN) magmeter Promag 10 inspected for accuracy every 6 months. All other measurements were done by taking samples to the on-site water quality lab transported on ice in coolers. Granular activated carbon (GAC) was acquired from the full scale system after being in use for over 2 years and had an effective size of 1mm. Because the GAC came from the full scale system, it was already bioactive. Anthracite was

acquired from Anthrafilter (Niagara Falls, NY). Since the anthracite had not been previously used, the filters were run for 3 months prior to performing any analysis. Velten et al. (2011) found that bioactivity reached a plateau (based on DOC removal and ATP analysis) after approximately 2 months. For the pilot study, filters 1 and 6 contained 24 inches of anthracite on top of 12 inches of sand. Filters 2, 3, 4, and 5 contained 24 inches of GAC on top of 12 inches of sand.

Backwash water was stored in a 1,000-L high density polyethylene (HDPE) tank. When chlorinated water was to be used for backwash, finished water from the clearwell of the full scale DLTWTF filled the tanks. When non-chlorinated water was to be used, effluent water from the pilot filters was collected and pumped into the tank.

Nutrient addition was accomplished using a 120-L HDPE tank combined with a Cole-Parmer MasterFlex peristaltic pump, with the nutrients feeding into the top of the filters. The ammonia solution was prepared from ACS grade ammonium chloride (NH_4Cl) (Fisher Scientific, Fair Lawn, NJ). The phosphorus solution was prepared from ACS grade 85% phosphoric acid (Fisher Scientific, Fair Lawn, NJ).

When the project first started, filters were manually backwashed twice a week (Tuesday and Friday) with their headloss recorded immediately prior to backwash. Starting in December of 2011, the filters were put on an automatic backwash sequence identical to the one outlined for the full scale DLTWTF filtration system in Chapter 2, using set points for run time, turbidity, and headloss identical to the full scale system. The run time set point was changed from 80 hours to 120 hours in April of 2012 to

accommodate increased filter run times. It was further raised to 150 hours in May of 2012. The backwash procedure consisted of first draining the filter water level to one foot above the media, followed by 90 seconds of air scouring at 3 scfm/ft^2. Low rate backwash at 7 gpm/ft^2 began in tandem with 45 seconds of air scouring. Low rate backwash continued for another 45 seconds, followed by 7 minutes of high rate backwash at 17 gpm/ft^2. High rate is followed by 1 minute of low rate backwash to finish the cycle. The filter is then put back in service.

3.2.2: Analytical Methods

Chloramine demand was measured by dosing waters with a 1.05:1 molar ratio of ammonia to chlorine at 8ppm chlorine through April 2011. After that, a molar ratio of 1.2:1 ammonia to chlorine was used due to breakpoint chlorination issues. To normalize samples, the volume each sample was adjusted to 1.8 L and the pH of each sample was adjusted to 7.70. Total chlorine was measured 45 minutes later after dosing. Following day one, total chlorine was measured daily at approximately the same time during the remaining four days by Standard Method 4500G-Cl Chlorine (Residual), DPD colorimetric method (Standard Methods 2005). Chlorine used for dosing was prepared from a 5-6% hypochlorite solution (Fisher Scientific, Fair Lawn, NJ). Ammonia used for dosing was prepared from ACS grade ammonium chloride (Fisher Scientific, Fair Lawn, NJ). Phosphate buffer solution and DPD indicator solution were purchased factory prepared (Ricca Chemical Company, Arlington, TX). Potassium iodide was prepared from ACS grade potassium iodide (Fisher Scientific, Fair Lawn, NJ).

Total organic carbon (TOC) was measured with a Teledyne Tekmar (Thousand Oaks, CA) TOC Fusion in accordance with Standard Method 5310C (Standard Methods 2005).

Assimilable organic carbon (AOC) was analyzed by MWH Laboratories (Monrovia, CA) following Standard Method 9217B (Standard Methods 2005). Carboxylic acids were analyzed according to an ionic chromatographic method reported by Peldszus et al. (1996), Kuo (1998), and Kuo et al. (1996) with minor modifications using an ion chromatograph method (Dionex ICS 3000) with details to be submitted for publishing. In summary, 20 ppm mercury chloride was used as a preservative and a sample holding time of 17 days was adopted. Post ozone samples were not aerated since ozone residuals were consistently close to non-detect. The calculated method detection limits (MDLs) were 3.7, 2.5, and 2.5 µg/L for acetate, formate, and oxalate, respectively. Carboxylic acids analysis beginning in May 2012 was performed by Underwriters Laboratory using the same method and instrument.

3.2.3: Experimental Design

Four major factors were evaluated for their potential efficacy in improving the performance of biofiltration. The first was filter depth, which was studied with GAC media at 24, 36, and 48 inches atop 12 inches of sand. The second condition was media material, replacing the GAC in filters 1 and 6 with anthracite. The GAC in filters 2-5 remained unchanged and the depth for all filters was adjusted to 24 inches. This allowed the next two conditions to be tested on both GAC and anthracite media simultaneously. The third condition was the effect of chloramines' presence in backwash water. To test this condition, the filters had to be run with non-chlorinated backwash water for an extended period of time (at least 1 month) to allow bioactivity to recover from regular chlorinated backwashes. Nutrient addition was studied with non-chlorinated backwash.

Ammonia and phosphorus were added to filters 1, 3, and 4 on the tops of the filters, allowing a comparison between GAC and anthracite.

During the course of each condition, samples were collected and tested for chloramine demand, TOC, AOC, and carboxylic acids. Samples were taken from before and after the pilot filters as well as from the full scale system, allowing a comparison of performance.

3.3: Results and Discussion

3.3.1: Chlorine Demand Background

As discussed in Chapter 2, high chlorine demand has been a persistent problem at the DLTWTF since ozonation and biofiltration were incorporated into the treatment plant. Chlorine demand is the amount of decay in chlorine concentration over a specified time period. At the DLTWTF, chlorine demand is calculated by the differences in chlorine concentration right after its addition at the plant and at the furthest end of the distribution system. Chlorine demand and chloramine demand are used interchangeably because chloramine is the only form of disinfectant present in the water. As a result, analytical procedures for total chlorine measurement were followed and the results should reflect chloramine levels.

Figure 3.1 shows the trend of total and distribution chlorine demand at the full scale DLTWTF system for 3 years. Total demand is the difference between the chlorine dosed at the plant and the chlorine residual at a remote location (longest residence time) in the distribution system. Distribution demand is the difference between the concentration at the entry point to the distribution system (the end of the clearwells) and the

concentration at the same remote location in the distribution system. Chlorine demand shows significant variation throughout the course of the year but without any consistent seasonal trend.

In Figure 3.1, the difference between total and distribution chlorine demand is the chlorine demand at the plant. With the worst case chlorine demand at the plant close to 5 ppm, it can create an operational challenge in addition to the increased chemical cost. In the ideal case, a much smaller and consistent difference between these two is desired, which is the case for non-problematic utilities. Degradation of the disinfectant residual in the distribution system always occurs, simply due to the amount of time water spends en route to customers, however it should be smaller too.

Chlorine demand between the dosing point and the entry point to the distribution system should be able to be reduced by improving the operation of biofiltration, leading to less compounds reacting with chloramine. While high chloramine demand is typically associated with high TTHMs production, the DLTWTF has not had TTHMs problems since the implementation of ozone and biofiltration, making the initiative for this project primarily a fiscal one. Fiscal benefits can be realized through two means: a decrease in the amount of chlorine and ammonia used for disinfection, and improved filter run times. Longer filter run times decrease the number of backwashes, reducing water and energy usage. Water for backwashing has been treated, so it carries with it the cost associated with treatment.

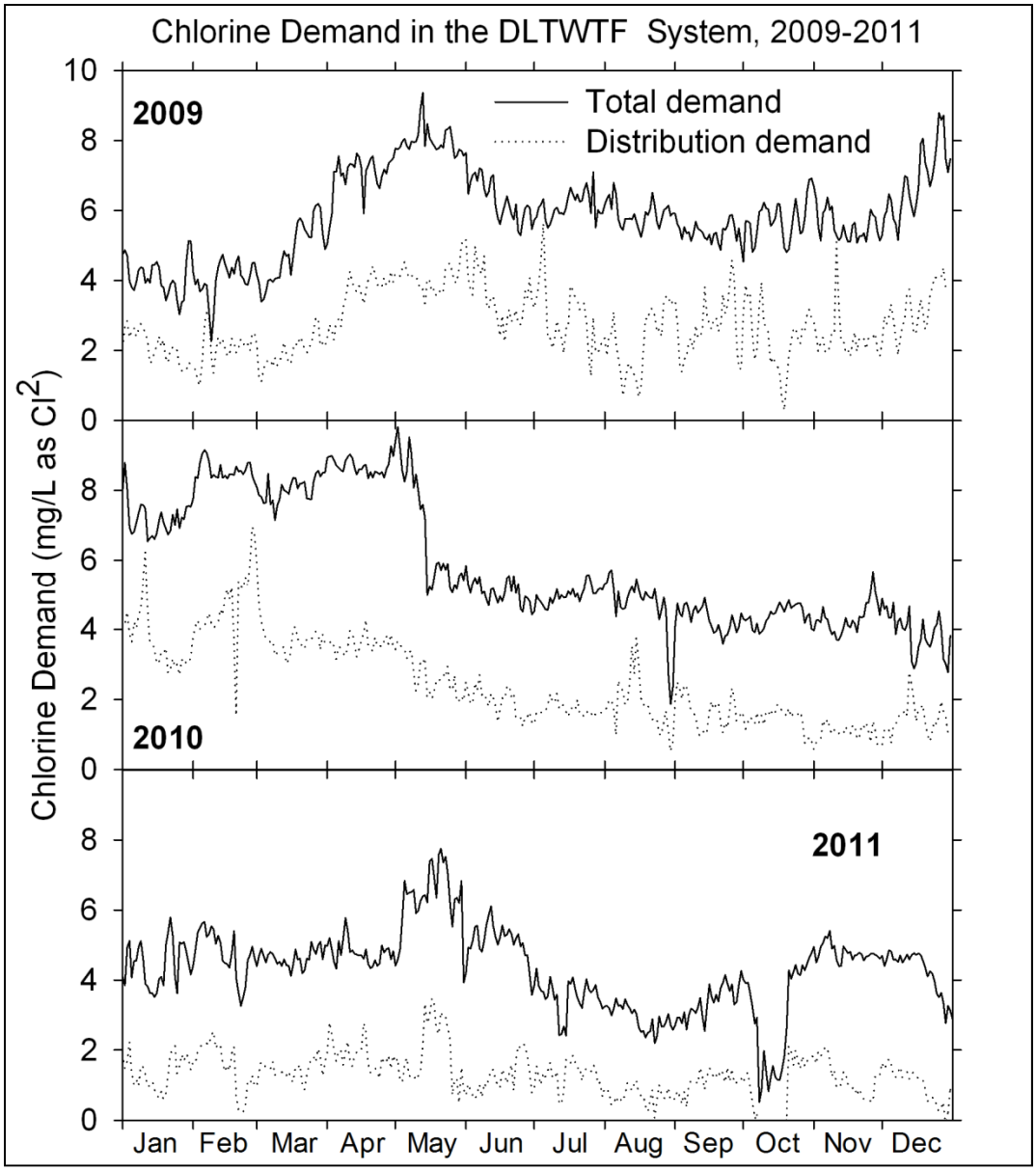


Figure 3.1: Chlorine demand at the DLTWTF for 2009, 2010, and 2011. Total demand refers to loss of chloramine from its application point at the plant to the furthest location in the distribution system. Distribution demand refers to loss of chloramine from the entry point to the same remote location in the distribution system.

Four different factors were evaluated for their effectiveness in improving biofiltration, using chloramine demand as a primary metric. Filter depth, media type, chlorination of backwash water, and nutrient addition were evaluated.

3.3.2: Filter Depth

The impact of filter depth on filter performance was investigated during the dry and wet seasons of 2009. The dry season study was performed in March and April, and the wet season in June, July, and August. Three filters were filled with 24, 36, and 48 inches of granular activated carbon (GAC) on top of 12 inches of sand. Filters were backwashed when they reached 7 feet of headloss. Filters were run at a loading rate of 2 gpm/ft^2. The influent TOC was 1.42 to 1.70 mg/L for the dry season and 3.51 to 3.61 mg/L for the wet season. Samples for the chloramine decay study were taken at specified amounts of time after backwash. For the wet season, samples were taken at five minutes, 1 hour, 3 hours, 8 hours, 24 hours, and 1 hour before the next backwash. The dry season was the same, except the last sample was taken at 48 hours after backwash.

Figure 3.2 shows the results of the chloramine demand samples. 24-inch and 36-inch filter depths had quite similar results during the wet season, but during the dry season the 24-inch filter had significantly higher chloramine demand. The 48-inch filter typically performed as well or slightly better than the 36-inch filter. All 3 configurations exhibited similar turbidity removal performance. Close to 80% of turbidity was removed at 5 minutes after filter backwash. Turbidity removal increased to over 90% in 30 minute samples and remained constant afterward. TOC removal is fairly constant at different filter run times for the same media depth. The TOC removals are similar between 24 and 36-inch GAC, with both exhibiting around 25% removals. The 48-inch GAC removed about 20% more TOC than the other 2 filter configurations.

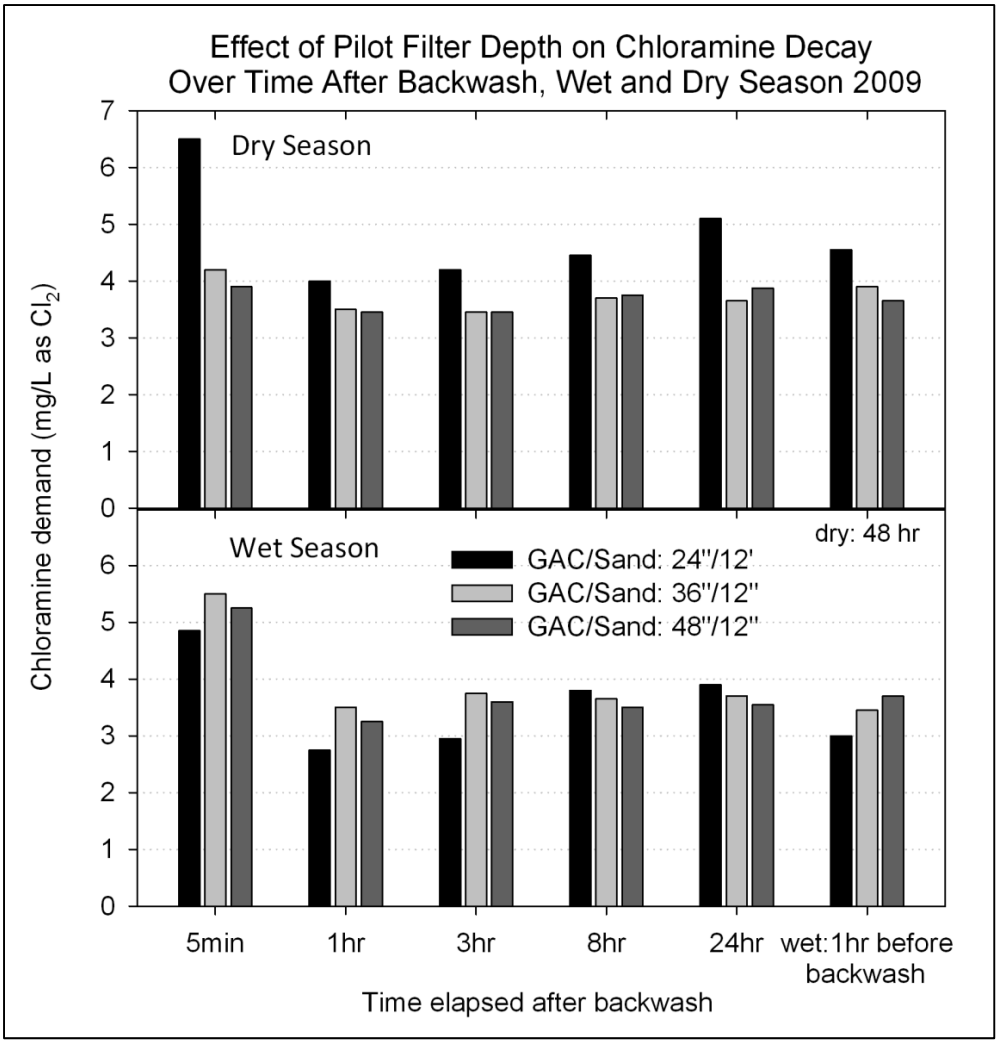


Figure 3.2: Effect of pilot filter depth on chloramine decay over time after backwash, wet and dry season 2009.

The turbidity removals were over 90% with the three filter configurations exhibiting similar efficacies for all samples collected at 30 minutes and afterward. As expected, a turbidity spike was observed for the 5-minute samples for all filters, a phenomenon typical of the filtration process. Overall, the increased performance of a deeper filter is quite small compared to the increased proportion of media required. At the DLTWTF, increased filter depth cannot be applied to the full scale filtration system without retrofitting the facility containing filtration despite the somewhat improved filter

performance. Deeper filters require higher air and backwash water flow rates to achieve similar fluidization levels, increasing costs and the likelihood of clogging.

3.3.3: Effect of Non-Chlorinated Backwash Water and Media Type

The effect of non-chlorinated backwash and media type was investigated with the 6 filters housed in the pilot plant. Two of the six filters contained 24 inches of anthracite on top of 12 inches of sand, and the other four filters contained 24 inches of GAC on top of 12 inches of sand. This allowed for the concurrent comparison of media types and backwash water. At the full scale DLTWTF, finished water with a typical chlorine residual of around 5 mg/L is used to backwash filters. Miltner et al. (1995) found that chlorinated backwash water could have a negative impact on biofilter performance. As chlorine is used to inactivate microorganisms in the distribution system, it is not surprising that it could have a negative impact on a biological process. To backwash with non-chlorinated water, a utility has to either collect filtered water before it is disinfected and store it for backwash later, or treat finished water with sodium bisulfite or other chlorine quenching compounds, leading to increased costs in either situation. At the pilot plant, filter effluent was collected and used to backwash the filters.

The analysis of three carboxylic acids, oxalate, formate, and acetate, was added as a metric. Carboxylic acids make up a varying percentage of AOC, and can be measured by a chemical method in 20 minutes as opposed to the 9 day biological method. Figure 3.3 shows the averaged total carboxylic acids removal by media type. Full scale performance is also displayed as a reference. Anthracite consistently underperforms GAC throughout all conditions in regards to TOC and carboxylic acids removal. Generally, carboxylic acids

removal stayed between 75% and 85% across all conditions and media type, with the pilot filters operating about the same as full scale and well within statistical error of each other.

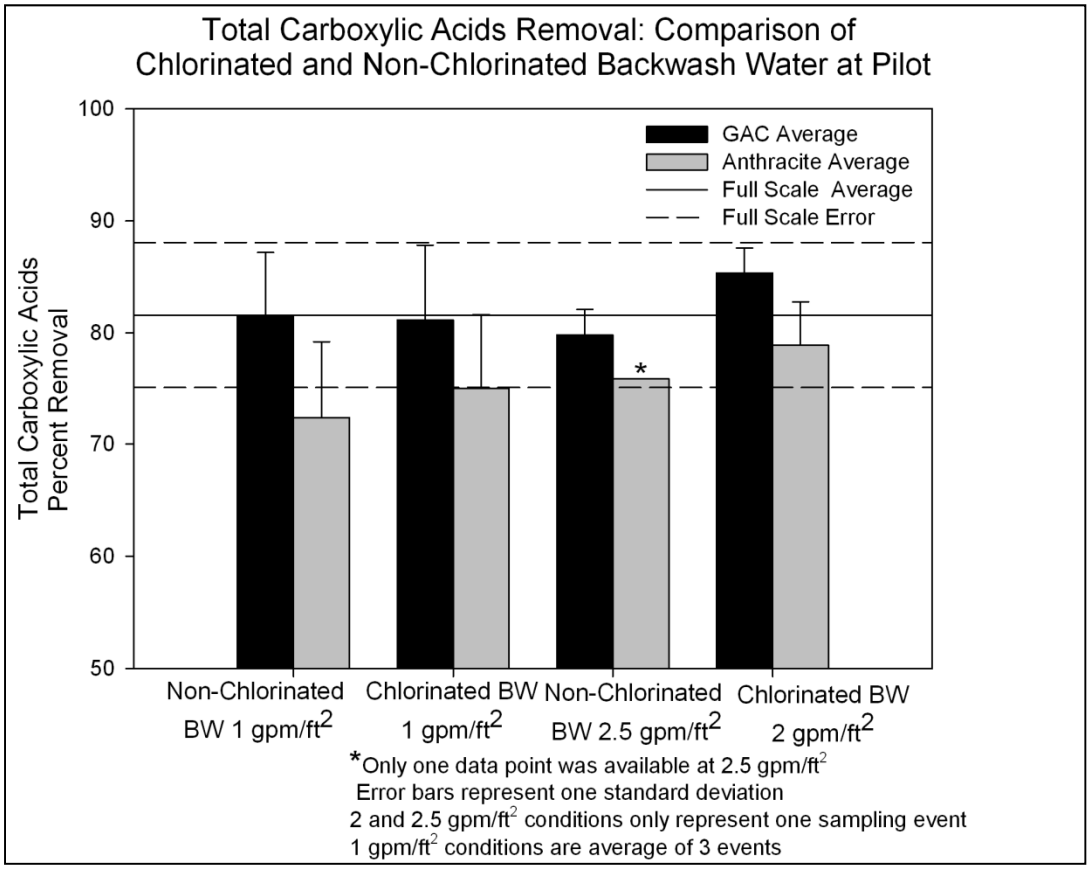


Figure 3.3: Total carboxylic acids removal: comparison of chlorinated and non-chlorinated backwash water

TOC removal was not as consistent as carboxylic acids removal. Similar to the carboxylic acids removal, anthracite performed worse than GAC for all conditions. Non-chlorinated backwash water appears to have a positive effect on TOC removal, especially compared to carboxylic acids removal. Increased loading rate decreases the performance of all filters under both conditions, with chlorinated backwash at a higher loading rate performing the worst. High loading rate did not affect carboxylic acids removal the way

it affects TOC removal. However, during the dry season, TOC is typically much lower in the raw water, leading to lower removal percentages. This could contribute to the significantly decreased performance of the 2 gpm/ft^2 chlorinated backwash condition and 2.5 gpm/ft^2 non-chlorinated backwash condition, which took place in December and October of 2011, respectively.

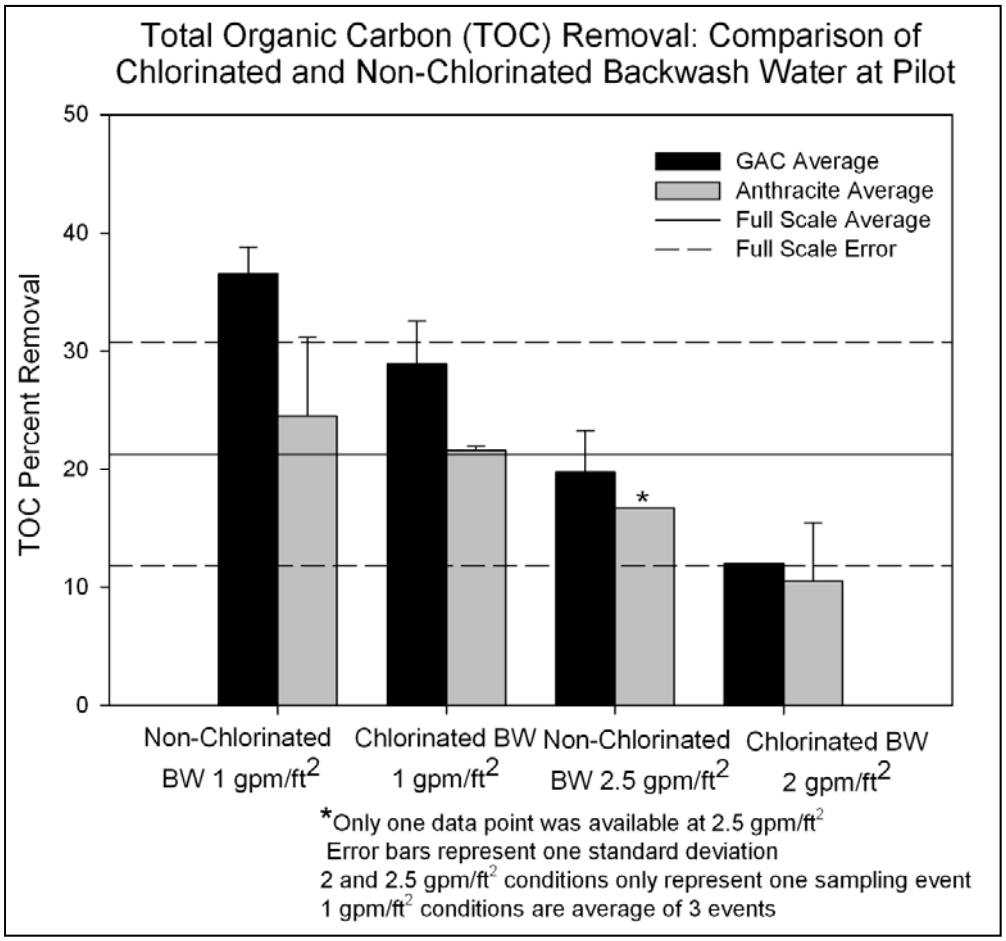


Figure 3.4: Total organic carbon (TOC) removal: comparison of chlorinated and non-chlorinated backwash water

Full scale samples taken as a reference to pilot samples during these two sampling events showed TOC removal percentages of 14 and 20 percent for December and October, respectively, which is also lower than the remainder of the year. This indicated

that the general dry season TOC removal trends are likely responsible for the decreased TOC removal performance for the two higher flow rate conditions. The advantage of GAC over anthracite in TOC removal is diminished at the two higher flow rates. This may be related to the dry season TOC removals, however. Similar to carboxylic acids removal, nearly every result is within the error range of the full scale system, showing that no condition performs extremely well.

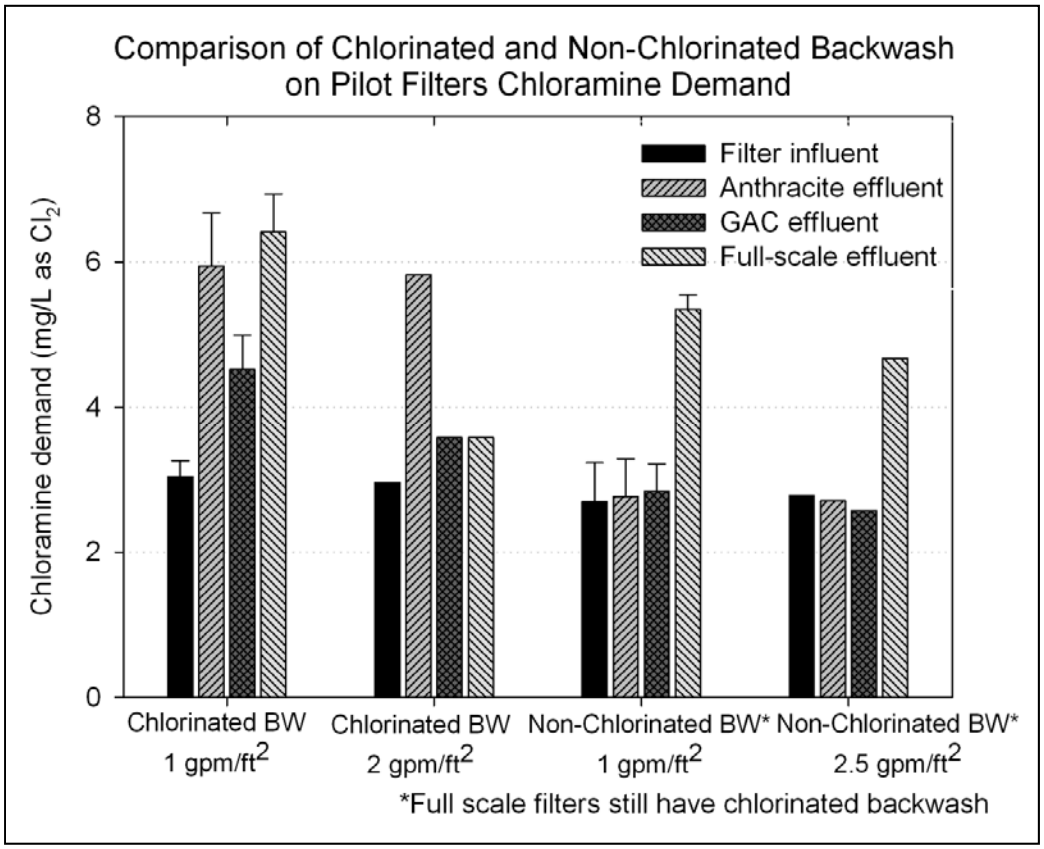


Figure 3.5: Comparison of chlorinated and non-chlorinated backwash water on pilot filters chloramine demand. Full scale demands are presented as a reference, backwashed with chlorinated water with loading rates between 1 and 3 gpm/ft^2.

Figure 3.5 shows the chloramine demand for the same conditions as shown in Figures 3.3 and 3.4. Compared to TOC removal or caryboxylic acids removal, non-chlorinated backwash water shows a pronounced effect on chloramine demand. Full scale and filter

influent chloramine demand are used as baselines for comparison. In an ideal system, biofiltration adds no additional chloramine demand to the water being treated. These results suggest that this is possible with non-chlorinated backwash water. When chlorinated backwash water is used, anthracite media performs significantly worse at both loading rates. No difference between anthracite and GAC is noticed at either low or high loading rates when non-chlorinated water is used. Anthracite performs approximately 50% worse with chlorinated water at the higher loading rates, with no performance change between loading rates when non-chlorinated backwash water is used.

Figure 3.6 shows the changes that take place in the TOC during the treatment process. Ozone breaks down the TOC, increasing the percent of AOC and carboxylic acids in the TOC. Biofiltration then preferentially removes the AOC and carboxylic acids, nearly reversing the increases in percentage created by ozone. The increases and decreases in AOC and carboxylic acids are proportional to one another, which is not surprising since carboxylic acids make up a portion of AOC. Carboxylic acids were used preferentially over AOC for comparison in this study due to the ability to analyze in house and the low number of samples tested for AOC.

Figure 3.7 illustrates the process used to determine chloramine demand, and portrays the similarity between the different filters. Initial chloramine concentration was measured 45 minutes after chloramine dosing, then measured again daily at the same time for the next 4 days, generating results like shown in Figure 3.7. Initial

measurements don't always match the concentration dosed, due to instantaneous chloramine demand and minute breakpoint chlorination from non-ideal mixing.

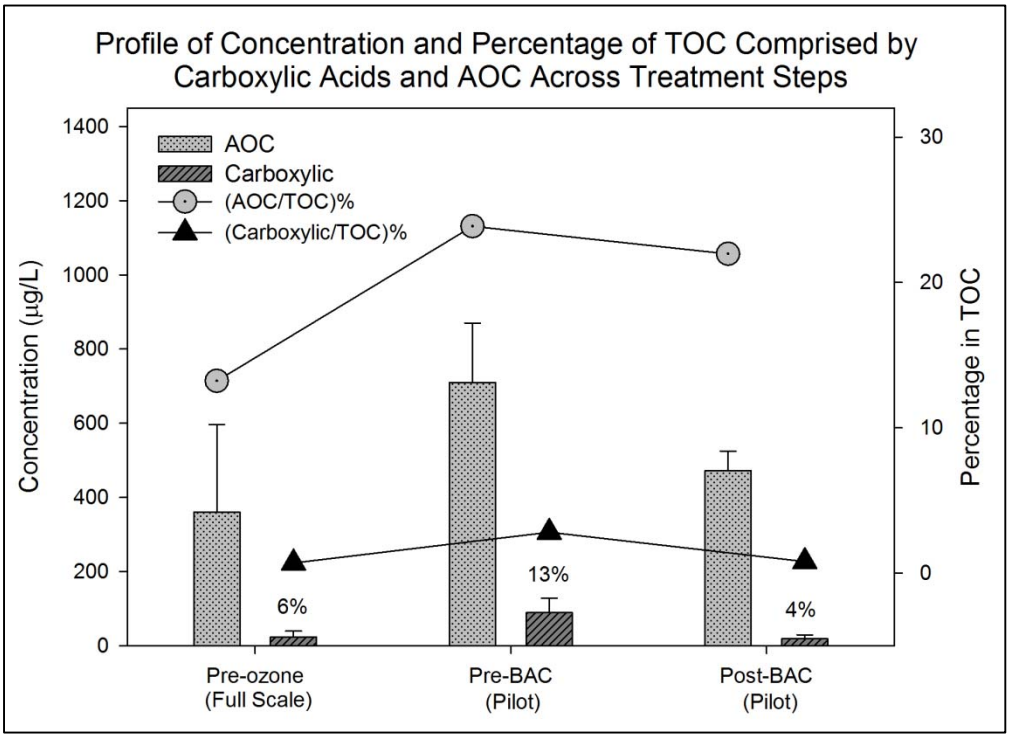


Figure 3.6: Profile of concentration and percentage of TOC comprised by carboxylic acids and AOC across treatment steps

As noted in Section 3.2.2, excess ammonia was increased to mitigate this. Under non-chlorinated filter backwash conditions, the effluent from both GAC and anthracite filters exhibited very similar chloramine decay profiles to each other and to the influent water. In the bottom left, a plot of the normalized decay curve further reveals the similarly between the filter media.

The performance of different filters is very consistent with non-chlorinated backwash, and chloramine demand seems to stay within a specific range. The error bars combined with the normalized graph in Figure 3.7 demonstrate this. However, this consistency in

performance applies only to chloramine demand, and does not exhibit itself for some other performance metrics such as filter run time, which will be discussed in further detail later on.

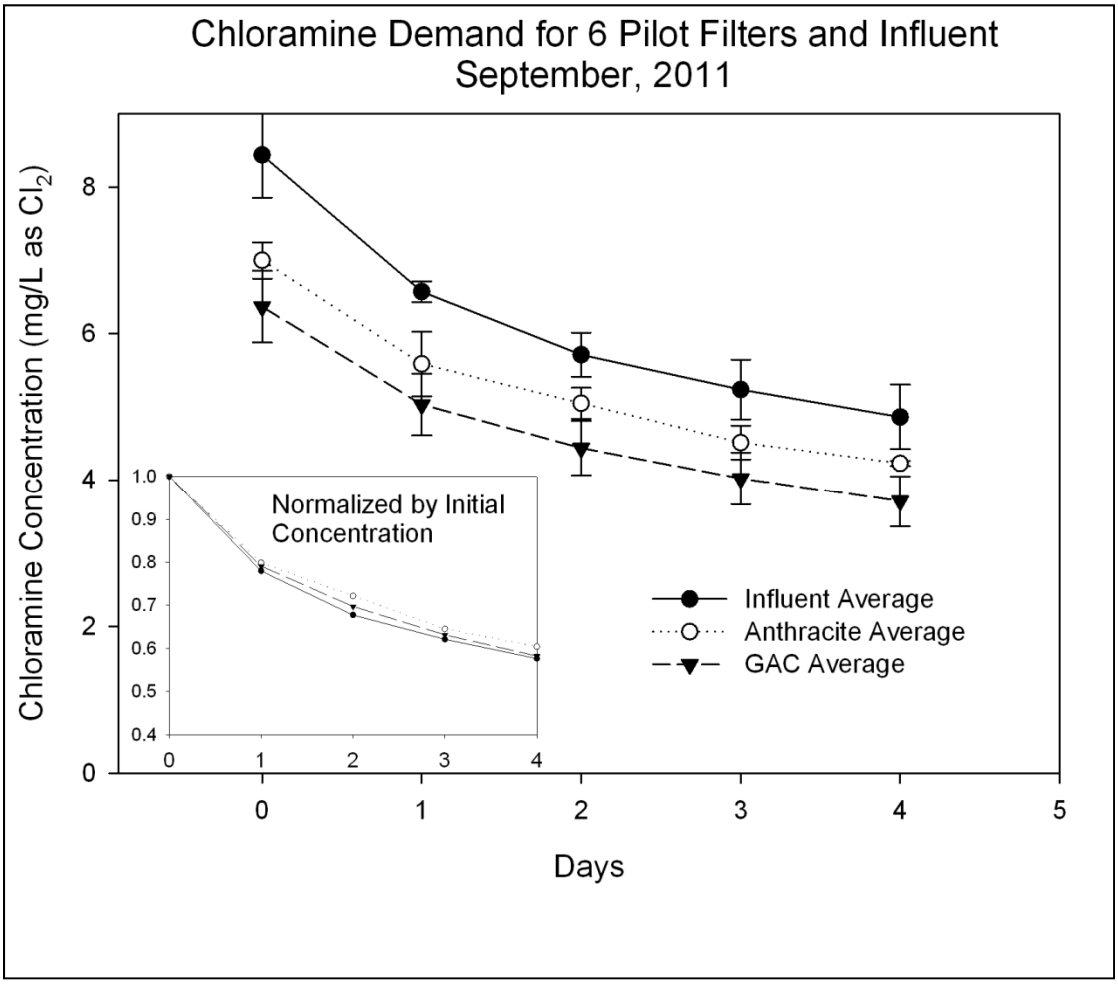


Figure 3.7: Chloramine demand for the influent and effluent of the 6 pilot plant filters with non-chlorinated backwash, September 2011

To elucidate the underlying mechanism for improved filter performance, the effluent from one GAC filter was treated by 0.45 micrometer filter and the difference in chloramine demand before and after filtration was studied under chlorinated and non-

chlorinated filter backwash conditions. The results are shown in Figure 3.8, normalized by initial concentration.

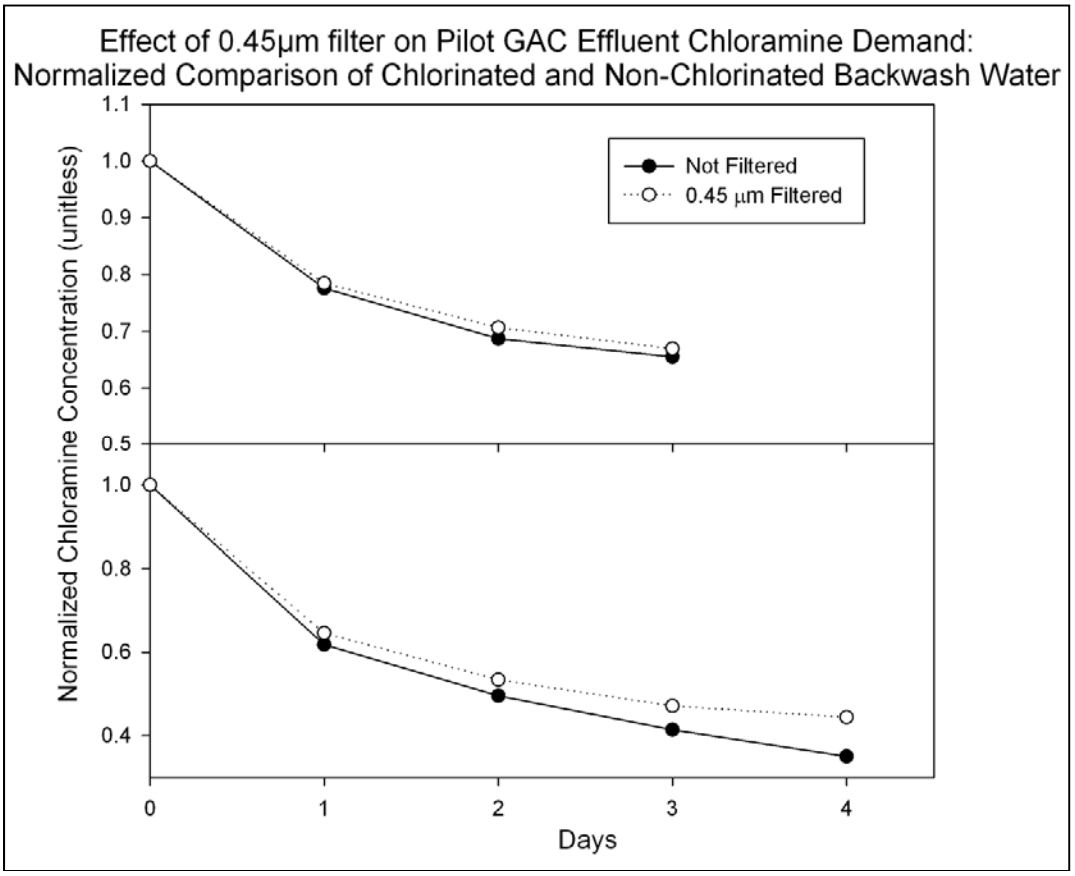


Figure 3.8: Effect of 0.45 µm filter on pilot GAC effluent chloramine demand: normalized comparison of chlorinated and non-chlorinated backwash water

When non-chlorinated backwash water was used, no discernible difference was noted after the sample was treated by the 0.45 µm filter. With chlorinated backwash water, the 0.45 µm filtration decreased chloramine demand significantly. On day 3, a 15% improvement was noticed, in contrast to the miniscule difference when non-chlorinated water was used for filter backwash. These results have suggested that particles small enough to avoid being retained by the GAC but large enough to be stopped by a 0.45 micrometer filter are the explanation for the improved chloramine decay.

3.3.4: Nutrient Addition and Filter Run Time

Beginning in May 2012, Filters 1, 3, and 4 had ammonia and phosphorus added to the tops of filters to test the effect that nutrient addition had on biofiltration performance. Concentrations were based on TOC using the 100:10:1 carbon:nitrogen:phosphorus molar ratio identified by LeChevallier et al. (1991) as the limiting ratios for biofilm formation in drinking water. Converting the ideal molar ratio of C, N and P of 100:10:1, the mass ratio of C, NH_4-N and orthophosphate-P is 1 mg/L : 0.117 mg/L : 0.026 mg/L. In 2009, the average TOC for post ozone was 2.6 ± 1.1 mg/L and in 2010 was 3.4 ± 0.5 mg/L. Using an average of 3.0 mg/L, the ratio is 3 mg/L : 0.351 mg/L : 0.078 mg/L. Ammonia and phosphorus were then added to the tops of the three filters at these concentrations. Figure 3.9 shows the results of nutrient addition.

For both GAC and anthracite columns, nutrient addition had no clear effect on TOC and carboxylic acids removal or chloramine demand. There may be a slight negative effect of nutrient addition on TOC removal, but it is within statistical error. The data suggests that carboxylic acids removal may be better with nutrient addition for anthracite, but with only one filter for nutrient addition for anthracite, a conclusion cannot be drawn.

Lauderdale et al. (2012) found that nutrient addition at the 100:10:1 carbon:nitrogen:phosphorus ratio decreased terminal head loss by 15% (meaning longer filter runtimes). They also found a decrease in dissolved organic carbon (DOC) for the filter effluent, which was not seen in this study for TOC. The hypothesis proposed by Lauderdale et al. (2012) states that the increased microbial activity due to nutrient addition is responsible for this phenomenon by decreasing EPS (which allows the filter to

run longer because it does not get clogged) and by providing the phosphorus and ammonia required for the utilization of carbon. Based on this hypothesis, the water at DLTWTF may have had sufficient nutrients to maximize performance already, and this is why no effect or a slight negative effect is observed.

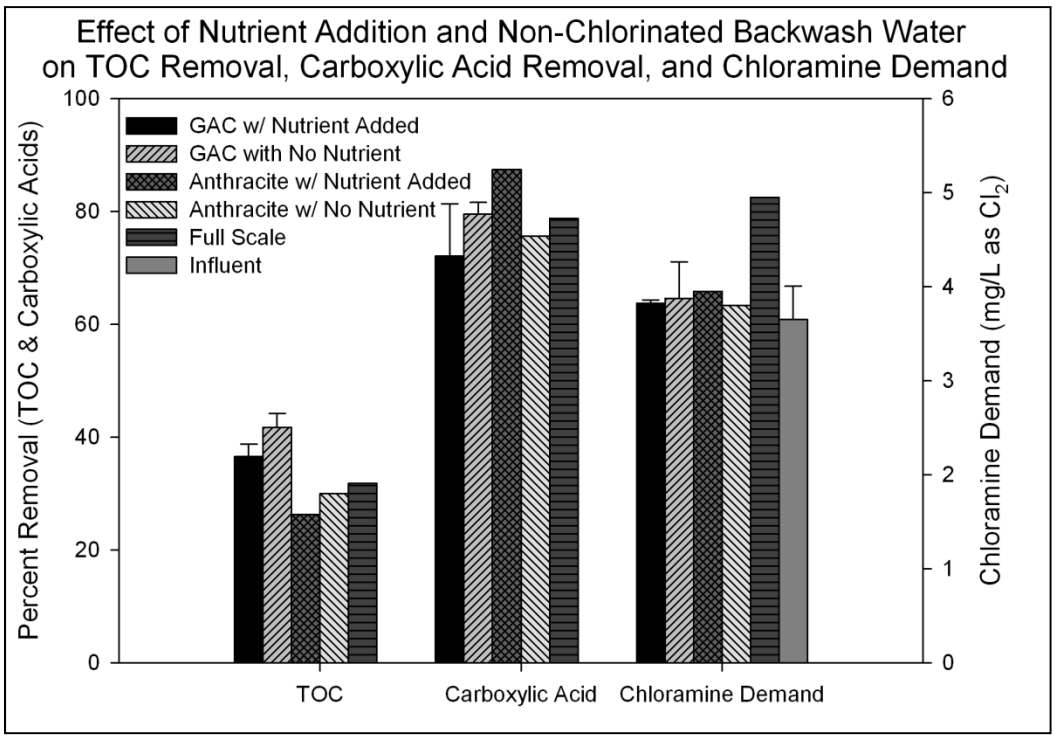


Figure 3.9 Effect of nutrient addition and non-chlorinated backwash water

Figure 3.10 shows the average filter run time for the pilot filters and full scale system at DLTWTF recorded since late 2011 when the pilot plant began to be backwashed by the fully automated SCADA system. No data on filter run time is available for most of 2011; because filters were manually backwashed one the same days twice per week and filter run time is not a possible parameter. With the implementation of automated backwash in late 2011, filter run time could be tracked to show the effect of different conditions. The results were summarized following the temporal order, divided by various testing conditions shown in the legend of Figure 3.10.

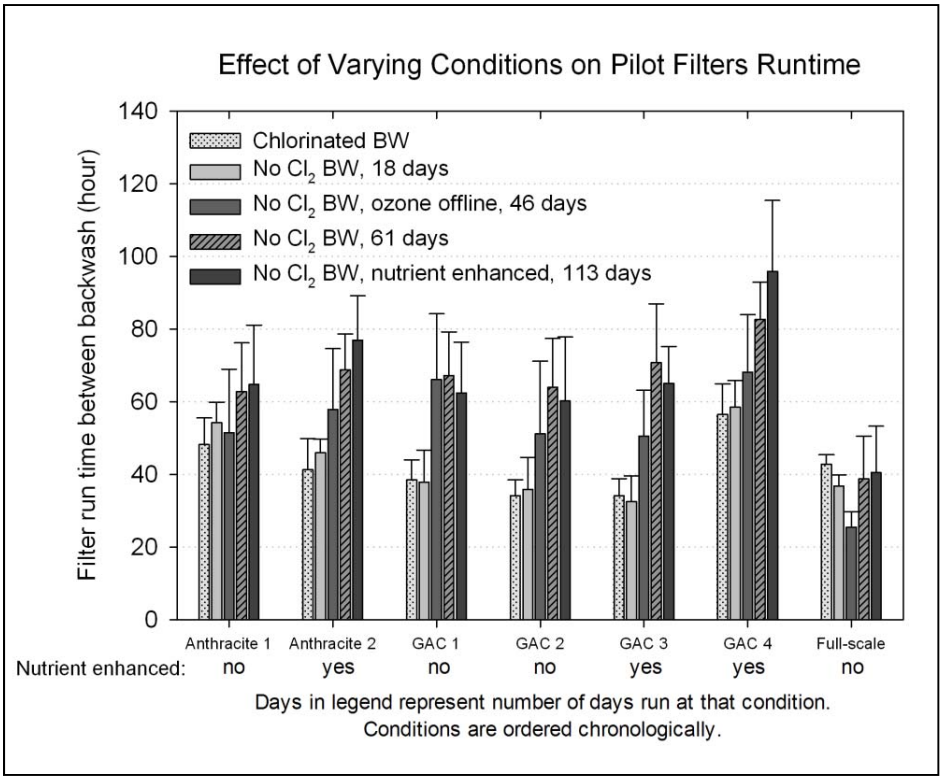


Figure 3.10: Effect of varying conditions on pilot filter run time

For anthracite media, nutrient addition appears to have a positive effect on filter run time; however GAC does not exhibit the same result. This could be due to the better biological activity and retention exhibited by GAC filters (Ahmad et al. 1998). GAC media may not benefit as much from nutrient addition because it is more likely that the bacteria have healthier colonies without additional nutrients. All of the pilot filters perform significantly better than the full scale system with respect to run time after the switch to non-chlorinated water. Since the increased performance is consistent across all filters, it's likely that the performance increase is related to non-chlorinated backwash water, not nutrient addition.

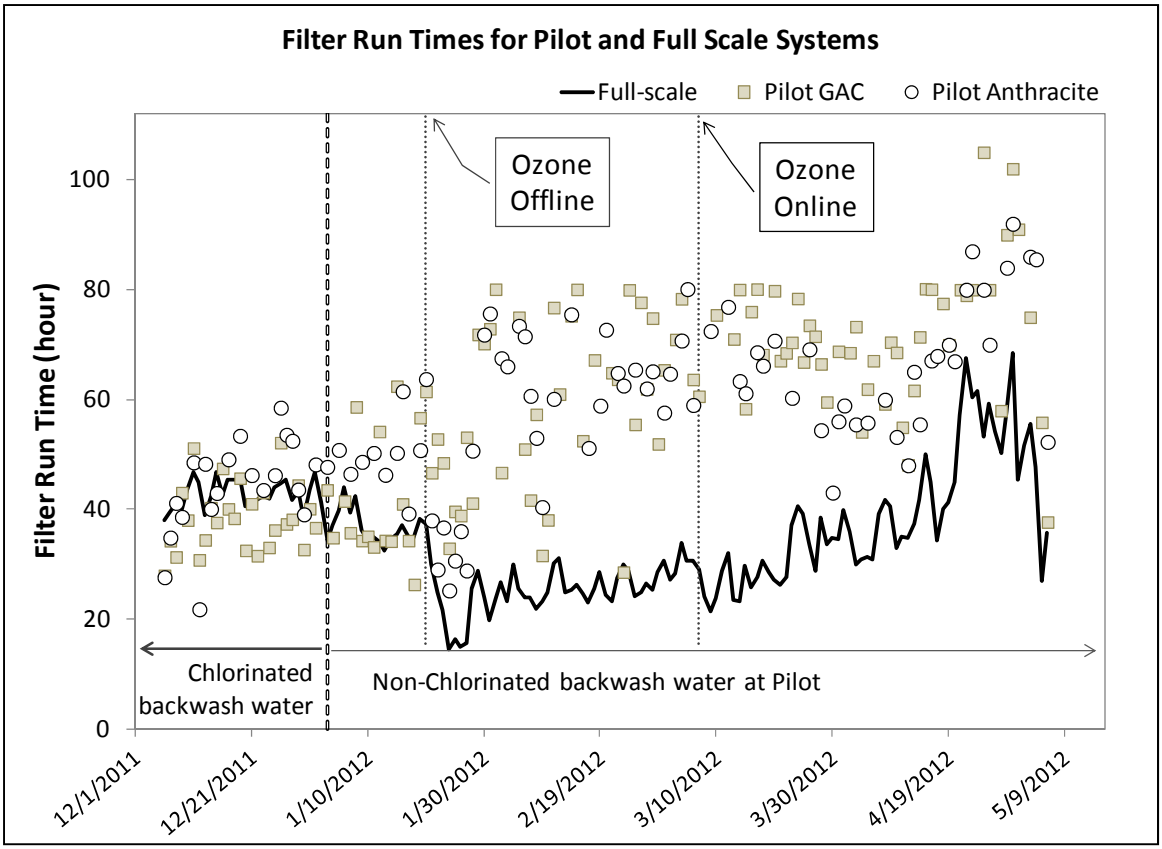


Figure 3.11: Filter run times for full scale and pilot systems

Figure 3.11 demonstrates the extreme variability of filter run time performance. The run times for pilot GAC came from the average of the four GAC filters and the anthracite results from the average of the two anthracite filters. Each filter not only differs by up to 50% compared to each other, each individual pilot filter's run times can vary by 20 to 30 percent between backwashes. It should be noted that despite the significantly different run time among the different filters, the chloramine demand and removal percentage sof TOC and carboxylic acids were very close under identical conditions. The data suggests that as run time increases, variance increases. Filter run time is very sensitive to variations in source water quality, with extreme peaks and falls within short time spans, compared to other metrics of filter performance.

3.3.5: Potential Cost Savings

Based on pilot plant study results, the estimated savings for chlorine and ammonia is about 20 to 30% depending on time of the year. Approximately one third of the savings is from ammonia and two thirds from chlorine, depending on current market prices. Additional savings should come from the lower amount of backwash water required due to longer filter run times. However, we have to include the cost of sodium bisulfite for quenching chlorine in the backwash water, which accounts for about 7% (assuming unit cost of sodium bisulfite is the same as chlorine). After adding in the cost of sodium bisulfite, the expected overall savings will be 13-23% of the chlorine and ammonia cost, which translates to $75,000 to $130,000 per year for chemical alone. More importantly, the biofilters will be optimized and pose less operational challenges. If filter effluent is collected and sodium bisulfite can be eliminated, the estimated cost savings will be 20 to 30% of chlorine and ammonia, which corresponds to $110,000 to $170,000 per year for chemicals alone. Assuming filter run times improve by 40%, 40% less backwash water will be required. This corresponds to approximately $120,000 additional savings from decreased backwash water, leading to a total savings of around $270,000 assuming the cost to produce water remains around $500 per million gallons.

3.3.6: Conclusion

The performance of biofiltration is affected by a multitude of factors, many of which have not been well studied or are not yet well understood. Based on the results of this study, increased bioactivity improves filter performance. The chlorination of backwash water has a strong negative effect on the performance of filters with respect to both

chloramine demand and filter run time. A switch to non-chlorinated backwash water will have the largest effect on a biofiltration system out of the factors studied, and subsequently will lead to the largest cost savings. Non-chlorinated backwash water results in effluent filter chloramine demand equal to that of the influent, representing a 50% improvement for anthracite and a 30% improvement for GAC. This improvement in chloramine demand results in a large cost decrease for chemicals. Non-chlorinated backwash water did not show any significant effects on TOC removal or carboxylic acids removal. An approximately 40% improvement in filter run time resulted from non-chlorinated backwash water, representing a 40% decrease in backwash water volume. Generally, GAC media performs better than anthracite media, but anthracite likely performs sufficiently for many utilities to consider it due to the significant cost difference between GAC and anthracite. This study showed no major effect from the addition of nitrogen and phosphorus.

Chapter 4: Bench Scale Evaluation of Chlorine-Ammonia Process for Bromate Control During Ozonation

4.1: Background

Potassium bromate ($KBrO_3$) was identified as a possible carcinogen in the early 1980s. It was first reported that oral administration of potassium bromate led to renal cell tumors in rats (Kurokawa et al., 1982) and further research showed that it was a probable carcinogen to humans (Kurokawa, 1990). As a result of this research, the EPA added bromate to a list of contaminants for consideration of regulation in 1994. In 1998, the EPA's Stage 1 Disinfection and Disinfection Byproducts Rule went into effect under the Safe Drinking Water Act, placing byproducts like trihalomethanes and haloacetic acids under more stringent regulation (EPA 1998). These regulations and their impacts are explored in Chapter 1 and the specific regulations of the Stage 1 DBP Rule are summarized in Table 1.1.

Ozonation started to become more popular in the United States as a disinfection method to meet higher disinfection requirements as well as increased taste and odor control, going from 40 ozone installations in 1991 to at least 264 in 1998 (EPA, 1999). The increasing market penetration of ozone combined with the new EPA regulations made bromate minimization increasingly important.

No effective and practical mechanism for the removal of bromate has been identified to date, forcing bromate reductions to happen through prevention of formation rather than removal in later process steps (von Gunten 2003, Kirisits et al. 2000).

The formation mechanism of bromate during ozonation is well studied and primarily consists of three pathways: the first is a direct pathway involving molecular ozone, and the second two are the direct-indirect pathway involving first molecular ozone and then hydroxyl radicals from ozone decomposition, and indirect-direct pathway where the hydroxyl radicals react first then the molecular ozone (Haag and Hoigné 1983, Song et al. 1997, von Gunten and Hoigné 1994). These pathways are illustrated in Figure 4.1. Von Gunten and Oliveras (1998) confirmed this bromate formation mechanism during ozonation of bromide containing waters based on laboratory experiments and kinetic modeling. Based on this mechanism, a study on the minimization of bromate reported the effects of ammonia addition, pH Depression, OH radical scavenging, and scavenging or reduction of hypobromous acid by organic compounds (Pinkernell and von Gunten 2001). Myllykangas et al. (1999) studied the effect of bromide ion concentration, pH, temperature, alkalinity, and hydrogen peroxide content on bromate formation, with only alkalinity having an effect. Galey et al. (1999) reported on the effect of acid addition and ammonia addition, finding both to decrease bromate, but with no increased combinational benefit. Berne et al. (2004) and Hofman and Andrews (2001) also elucidated the effect of ammonia and bromamines on bromate reduction. A novel approach using a chlorine-ammonia process was developed using a bench scale batch ozonation system and its efficiency studied at varying pH, ozone exposure, and chlorine concentration (Buffle et al. 2004). Wert et al. (2007) confirmed the efficacy of the

chlorine-ammonia process for bromate reduction in a pilot scale ozonation system using Colorado River Water and validated the pilot results with full scale implementation.

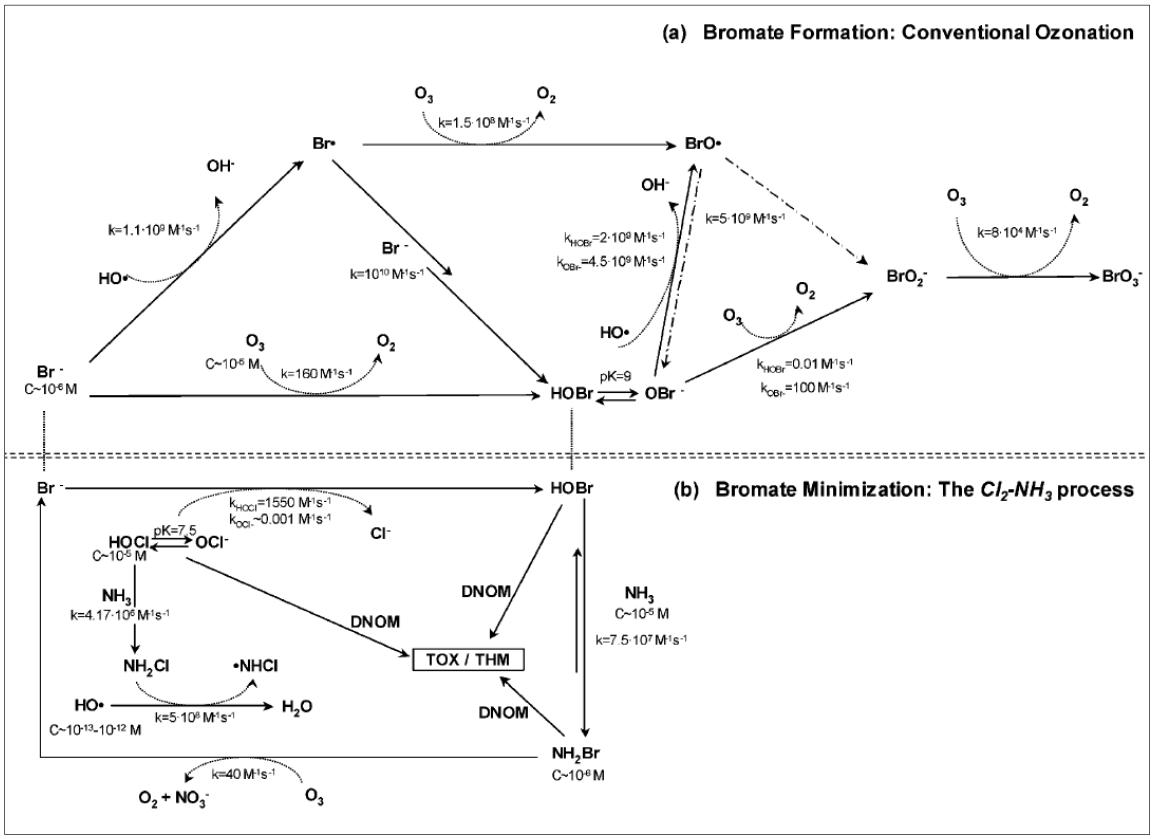


Figure 4.1: Key reactions involved in bromate formation. (a) Bromate formation during conventional ozonation (b) Reactions induced by prechlorination and ammonia addition during the Cl2-NH3 process. Adapted with permission from Buffle, M.-O.; Galli, S.; von Gunten, U., Enhanced Bromate Control during Ozonation: The Chlorine-Ammonia Process. Environmental Science & Technology 2004, 38 (19), 5187-5195. Copyright 2004 American Chemical Society.

Bromate is formed through a multi-stage, multi-path oxidation process from the bromide ion, described in Figure 4.1a. Bromate requires a strong oxidant to be formed, and cannot be formed by oxidation by hypochlorite. The primary bromate control mechanisms in water treatment at a given concentration of bromide are pH depression, ozone exposure reduction, and the chlorine-ammonia process. Reducing ozone exposure

is the simplest and most effective method, as it removes the oxidative capacity of the system, but it is also the least desirable protocol in water treatment since ozone is used for disinfection or taste and odor control. Lowering pH increases the scavenging of OH radicals, which leads to less Br• formation and hence reduces the concentration of OBr^- relative to HOBR, preventing the pathway from BrO_2^- to bromate. The chlorine-ammonia process described in Figure 4.1b reduces bromate formation by reducing the amount of bromide that can be oxidized to bromate. First, the chlorine oxidizes the bromide ion to HOBr, which then reacts with ammonia to form NH_2Br. The bromamine will subsequently react with organic matter or be oxidized to nitrate and bromide. Ammonia can be used to reduce the formation of bromate on its own by converting a small amount of bromide to bromamine, but the effect is much more pronounced using both chlorine and ammonia.

Built in 1924, the David L. Tippin Water Treatment Facility (DLTWTF) currently treats water from the Hillsborough River Reservoir in Tampa, Florida. Chapter 2 discusses the details of operation and treatment and Figure 2.1 depicts the general treatment process. During the wet season (June-September), extra water is treated and pumped into a series of Aquifer Storage and Recovery (ASR) wells. ASR water is then pumped back out during the dry season (October-May) to supplement water supply. The high dissolved oxygen content of finished water pumped into the ASR wells frees bromide from the geological formation. The increased bromide from the ASR wells increases the total bromide in the feed water to a level where bromate formation during ozonation approaches or exceeds the EPA's maximum contaminant level (MCL) of 10 ppb on an annual average. Traditionally, pH was used as the primary control strategy. A decrease

in pH inhibits bromate formation, however, pH depression prior to ozonation is operationally expensive at DLTWTF. After enhanced coagulation/flocculation, the pH is already quite low, and lime (calcium hydroxide, $Ca(OH)_2$) is used to raise the pH to 6.5 before ozonation. After ozonation, caustic soda (sodium hydroxide (NaOH)) must be used for any further pH increases, as lime will cause turbidity issues downstream in the filters at this application point. Lime is desired over caustic soda because it has a fourfold advantage, because it costs half as much, and its bivalent nature makes it twice as effective. For this reason, the chlorine-ammonia process was investigated due to its ability to keep bromate production below the MCL as well as increase the use of lime by raising the pH of the ozonation process.

4.2: Materials and Methods

4.2.1: Reagents

Indigo stock solution consisted of 0.770 g of potassium indigo trisulfonate (Sigma Aldrich, St. Louis, MO) and 1 ml of 85% HLPC grade concentrated phosphoric acid (Fisher Scientific, Fair Lawn, NJ) per one liter of solution. The stock was stored in an amber bottle for less than four months. The indigo reagent solution consisted of 50 mL of the indigo stock solution, 11.5 g of sodium phosphate monobasic monohydrate (Sigma Aldrich, St. Louis, MO), and 7.0 mL of HPLC grade concentrated phosphoric acid (Fisher Scientific, Fair Lawn, NJ). It was stored in an amber bottle for less than one week. 100 mg/L bromide stock was created by diluting 1000 ppm bromide stock solution (NSI Solutions, Raleigh, NC). 400 ppm ammonia stock contained 1529 mg of ammonium chloride (Fisher Scientific, Fair Lawn, NJ) per liter of solution. Chlorine stock had a target concentration of 600 ppm, and was made by adding 11 mL of 5-6% hypochlorite stock

solution (Fisher Scientific, Fair Lawn, NJ) to one liter of water. Chlorine stock solution concentration was tested weekly to determine if the concentration remained steady. All solutions were prepared with distilled deionized water (DDI water) prepared by an Ultrapure (Dallas, TX) deionization system with a resistivity above 18 MΩ·cm. Ozone stock solution was created by dissolving a mixture of ozone and oxygen gas generated by an A2Z Ozone Generator model A2ZS-16GLAB operated at 50% capacity and one liter per minute oxygen flow rate into DDI water using a Fisher Scientific coarse gas wash bottle. Off gas was treated with a sodium thiosulfate solution for quenching. The gas wash bottle was placed in an ice bath prior to generation. The generator was run for 30 minutes to achieve a steady state solution.

4.2.2: Experimental Methods

A 100-ml SGE gastight syringe was used as the reactor vessel in all experiments. The syringe was placed inside of a water bath which was maintained at 20^{o}C. The syringe was connected to the outside of the water bath using 1/16 inch diameter 316 stainless steel tubing with a Swagelok valve to control flow. A luer-lok needle with 1/16 inch diameter was used as the direct connection to the syringe and to the outside of the water bath. Figures 4.3 and 4.4 show the apparatus used in this study.

Prior to each experiment, the pH of the water to be used in the experiments was adjusted to 7 using hydrochloric acid or sodium hydroxide with a Thermo Scientific ROSS ORION pH probe. Bromide stock was added at this time. After pH adjustment, the sample was placed in the reactor. The plunger was removed to add the sample, the syringe was filled to the top and then the plunger was pushed in to ensure no air was in

the syringe. A stir bar placed inside the reactor was stirred by a waterproof stir plate inside the water bath. The volume inside the reactor was adjusted to 85 mL.

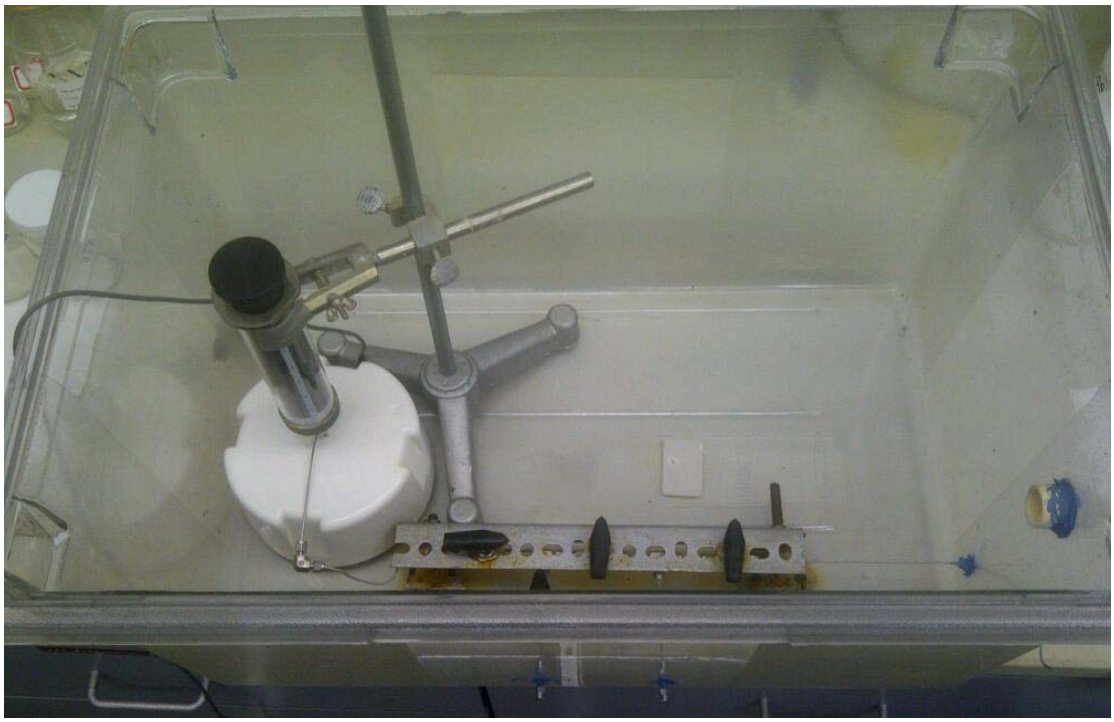


Figure 4.2: Picture of apparatus used for the bench scale bromate study

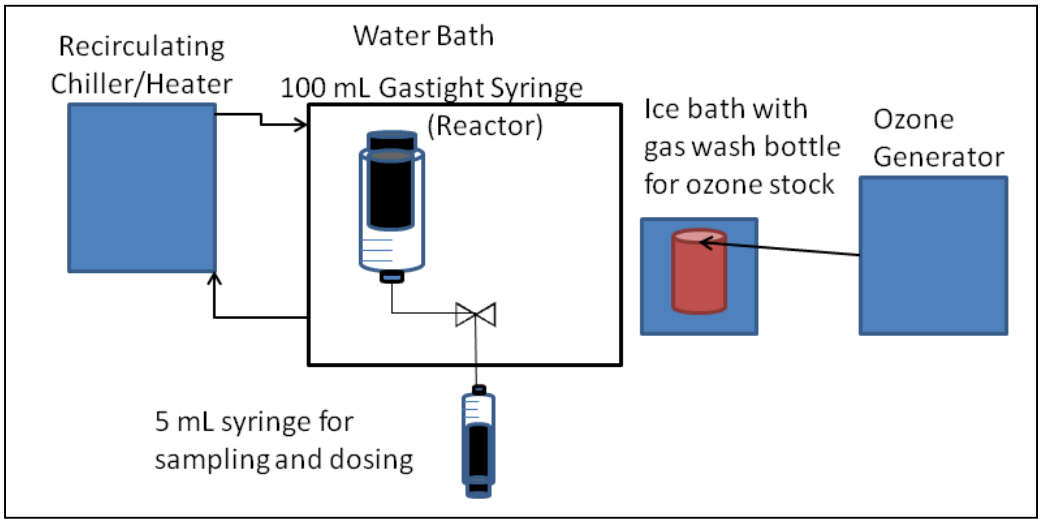


Figure 4.3: Diagram of apparatus used for the bench scale bromate study

Some of the sample was retained in a 5-ml syringe for final volume adjustment. After approximately ten minutes (allowing temperature to adjust from room temperature), chlorine was added in the appropriate dose using a 500-µl SGE gastight syringe. Approximately 1 ml of the retained sample in the second syringe was used to flush the chlorine from the tubing into the reactor. After five minutes, the ammonia was added in the appropriate dose and flushed into the reactor using the same syringes and process. One minute after the ammonia dosing, 7-8 mL of ozone stock solution was added to the reactor. The stock was then flushed out of the tubing and the volume adjusted to exactly 100 mL using the 5-ml syringe. 5-ml SGE gastight syringes were used to pull ozone samples from the reactor. They were prefilled with three milliliters of indigo reagent solution. Samples were taken every minute for the first ten minutes and varied after ten minutes until the ozone concentration was 0.1 mg/L or below.

4.2.3: Analytical Methods

Dissolved ozone was measured on a Thermo Scientific Aquamate VIS model 9423AQA2600E using a modified Standard Method 4500-Ozone (Standard Methods 2005). Indigo reagent is rapidly decolorized by ozone, and the Standard Method was adapted to allow for varying volumes of samples and Indigo reagent. The derivation is included in the appendix. Using 2 ml of sample and 3 ml of indigo reagent, the typical measurement range of the concentration was 0-3.5 mg/L of ozone; the range varied from day to day based on the absorbance of the indigo reagent. Bromate analysis was performed on a Dionex Ion Chromatography ICS 3000 with an AS19 Column using conductivity detection, an injection volume of 1000 µL, and 9-10 minute retention time using EPA Method 300.1. The ozone decay curve was generated by plotting ozone

residual versus time to allow the calculation of CT (ozone concentration x contact time). The trapezoidal numerical method was used for the calculation and is explained in Figure 4.5.

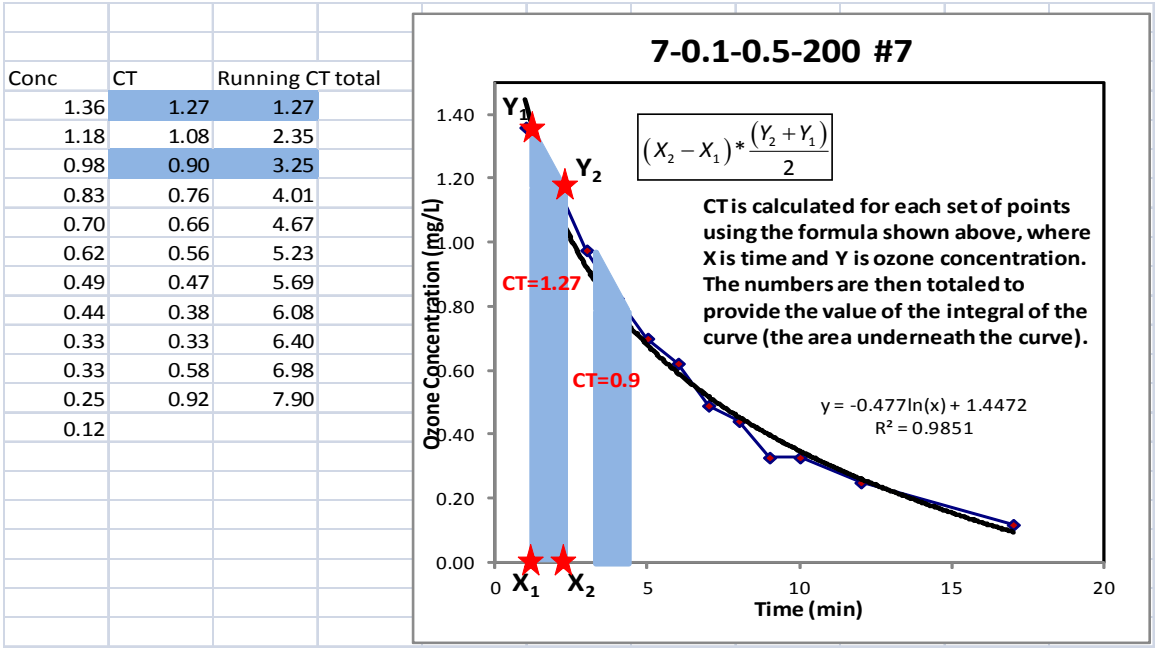


Figure 4.4: Example of CT calculation

4.2.4: Experimental Design

Table 4.1 shows the labeling identification used for each condition examined in the experiments of this study and the associated pH, bromide concentration, chlorine concentration, and ammonia concentration. Three different chlorine concentrations were used with various ammonia levels for each chlorine concentration.

Table 4.1: Experimental matrix used for bromate control study

ID (pH-NH3-Cl2-Br)	pH	Final Bromide Concentration (ppb)	Chlorine (mg/L as Cl_2)	Ammonia (mg/L as NH_3-N)
7-0-0-200	7	273	0	0
7-0.1-.25-200	7	273	0.25	0.1

Table 4.1 (Continued)

7-0.2-0.25-200	7	273	0.25	0.2
7-0.3-0.25-200	7	273	0.25	0.3
7-0.1-0.5-200	7	273	0.5	0.1
7-0.3-0.5-200	7	273	0.5	0.3
7-0.5-0.5-200	7	273	0.5	0.5
7-0.15-0.75-200	7	273	0.75	0.15
7-0.3-0.75-200	7	273	0.75	0.3
7-0.45-0.75-200	7	273	0.75	0.45
7-0.6-0.75-200	7	273	0.75	0.6

Bromate formation was investigated with the bench-scale set up described in the Experimental Methods section. A pH value of 7.0 was selected as an improvement of the pH of 6.5 typically implemented at the full-scale plant in order to lower the cost of caustic soda, in addition to the benefit of better bromate control. When pH is increased before ozonation, lime can be used at a fourfold cost advantage over caustic soda. The testing water was collected before ozonation from the full-scale plant on October 24th, 2011. The water was analyzed for Total Organic Carbon (TOC) (4.1 mg/L), bromide (73 ppb), bromate (non-detect), calcium hardness (124 mg/L), ammonia (0.1 mg/L NH_3-N), UV-254 (0.06) and alkalinity (48 mg/L as $CaCO_3$).

Baseline conditions at pH 7.0 without any chlorine or ammonia addition and bromide spiked at various concentrations were studied first to establish the baseline bromate formation without any optimization. The experimental matrix for the bromate control study consisted of varying the levels of ammonia and chlorine with bromide spiked at 200 ppb. The water before any chemical addition already had 73 ppb bromide naturally, leading to an actual value of 273 ppb after the addition of bromide. During the dry season, the bromide level before ozonation is typically between 200-400 ppb, so 273

ppb was chosen to represent conditions for the full scale plant. The rest of the matrix varied ammonia for three distinct groups of chlorine concentrations using ratios similar to Wert et al. (2007).

Ozone dose was selected to achieve a CT within the range of the full scale plant. The ozonation at DLTWTF full-scale plant consists of 2 parallel independent channels, with each processing half of the total flow. Each channel has internal baffles that divide the channel into 8 cells with water going in from cell No. 1 and leaving from cell No. 8. The ozone concentrations at each channel were monitored by online ozone analyzers continuously at the effluent end of cells 2, 5 and 8. These 3 ozone concentrations were averaged between the 2 channels and used to derive ozone decay rate assuming first order kinetics. The resulting regression coefficients spanned over the range of 0.88 to 0.99. Subsequently the theoretical ozone residual at each cell could be derived and integral of CT (ozone concentration × time) over the entire ozone contact chamber calculated based on hydraulic retention time and effluent ozone residual of each cell. The CT of the full scale system typically falls in a range from 4-7 min·mg/L, so this was the ideal range used for the bench scale testing.

4.3: Results and Discussion

To show the general relationship between bromate, bromide, and ozone dose, full scale data from the DLTWTF is provided in Figure 4.6. As seen in this figure, the general trend of bromate increases when either bromide or ozone demand spike is clear. Ozone demand is the difference between the ozone dosed and the ozone concentration in cell 5. Ozone demand increases during high TOC and high color events. While pH has a

large effect on bromate production, it is not included in the graph because it is fixed to a tightly controlled range (6.2-6.5) to prevent bromate formation in the full scale plant, making it difficult to see any relationship between pH and bromate formation. TOC ranges from 1-5 mg/L, cycling seasonally with the highest range during the rainy summer season, and lowest during the dry winter. Flow rate is also a seasonal trend, ranging from a dry season low of around 60 MGD to a wet season high of 100 MGD. Bromide conversion to bromate averages 1.8% during the dry season and 3% during the wet season.

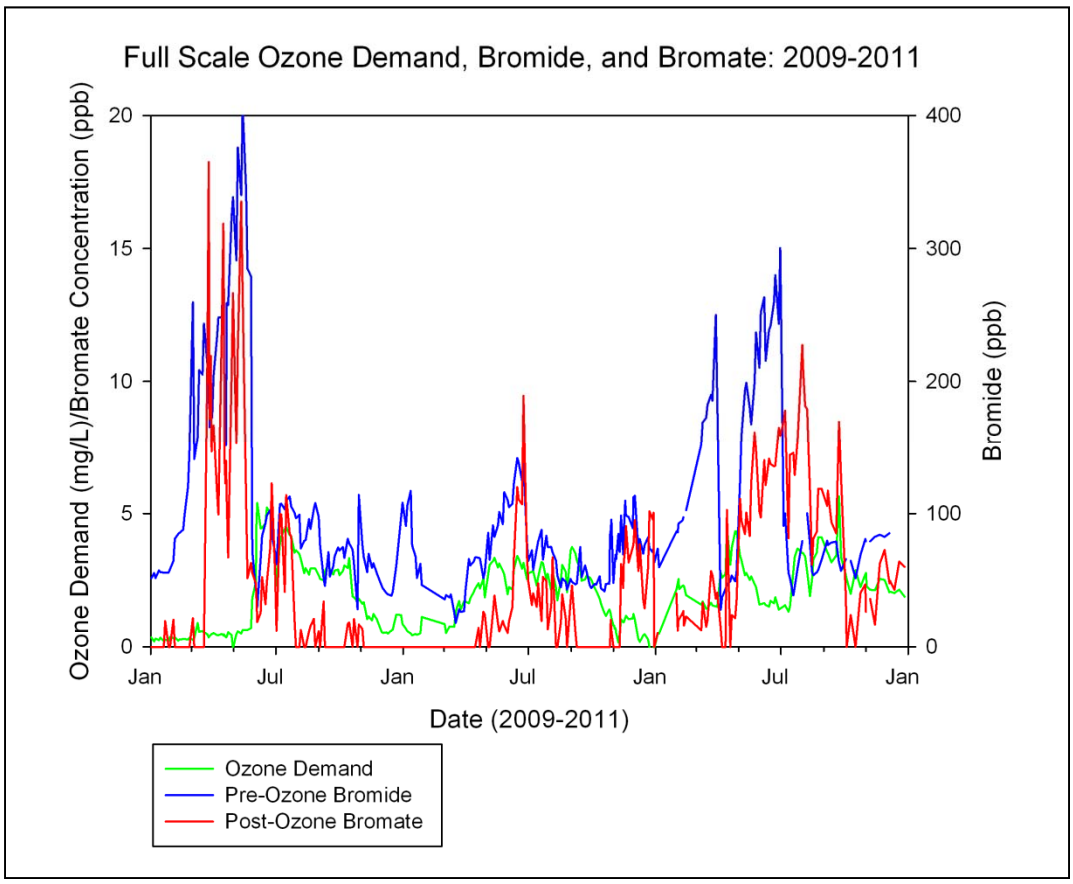


Figure 4.5: Full scale ozone demand, bromide, and bromate at the DLTWTF from 2009 to 2011.

Each condition was run with at least 2 replications and the actual CT calculated based on the ozone decay curve, which varied from the target CT to various extents. To compare the results between replications, bromate values had to be normalized using CT. A linear regression was performed for each set of replicates. A CT inside the range of CTs for each replicate was used to predict the bromate level at a CT that can easily be compared to other sets. For this reason, it is important to note the 'CT' value next to each 'CT Adjusted Bromate' value in Table 4.2 showing the results. All bromate numbers could not be adjusted to the same CT because the relationship between CT and bromate is not a perfect linear relationship, and thus extrapolation is inaccurate, but interpolation can give us a reasonable estimate. An example of this process is displayed in Figure 4.6.

ID	Bromate	CT
7-0-0-200 #1	6.18	3.79
7-0-0-200 #2	5.23	5.26
7-0-0-200 #3	4.73	3.48
7-0-0-200 #4	7.42	6.36
7-0-0-200 #5	10.54	8.50

Adj Bromate =
1.0332*(5.8)+1.1622=7.58

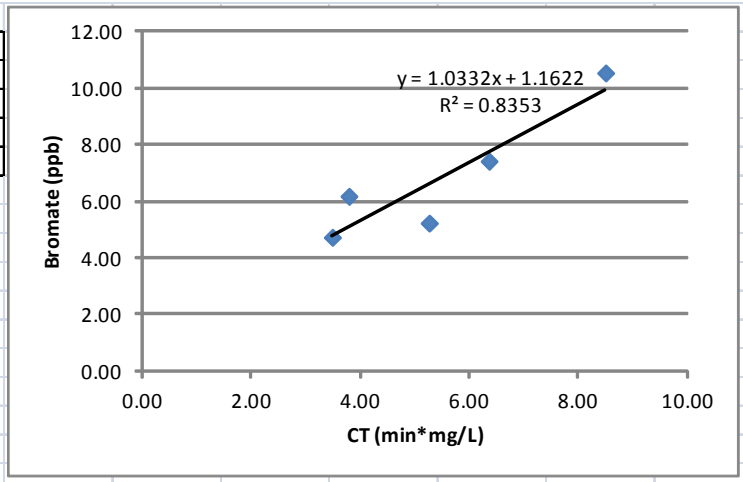


Figure 4.6: Example of adjusted bromate calculation

After adjusting each data set to a CT within range, a CT adjusted bromate value can be calculated. We can then compare all the variations of the experiment to a certain extent. The groups at 0.25 mg/L and 0.5 mg/L Cl_2 all had CTs within a certain range, and were able to be adjusted to 5.3 min·mg/L and 6.2 min·mg/L, respectively. The data for 0.75 mg/L Cl_2 did not have consistent enough CTs to allow for this, so a CT for each condition

had to be used. A higher CT leads to a higher bromate concentration. Because of this, 7-0.45-0.75-200 below is likely a significantly better control measure compared to 7-0.3-0.75-200 due the nearly identical bromate value, but a significantly higher CT value.

Table 4.2: Final results of bromate control study

ID (pH-NH3-Cl2-Br)	pH	Final Bromide Conc (ppb)	Chlorine (mg/L as Cl_2)	Ammonia (mg/L as NH_3-N)	CT Adjusted Bromate (ppb)	CT (min*mg/L)
7-0-0-200	7	273	0	0	7.58	5.8
7-0.1-.25-200	7	273	0.25	0.1	3.66	5.3
7-0.2-0.25-200	7	273	0.25	0.2	2.81	5.3
7-0.3-0.25-200	7	273	0.25	0.3	2.36	5.3
7-0.1-0.5-200	7	273	0.5	0.1	3.27	6.2
7-0.3-0.5-200	7	273	0.5	0.3	3.53	6.2
7-0.5-0.5-200	7	273	0.5	0.5	3.18	6.2
7-0.15-0.75-200	7	273	0.75	0.15	2.90	6
7-0.3-0.75-200	7	273	0.75	0.3	1.05	5
7-0.45-0.75-200	7	273	0.75	0.45	1.09	6.8
7-0.6-0.75-200	7	273	0.75	0.6	1.60	5.9

The least effective ammonia-chlorine dosing regimen resulted in an over 50% reduction in bromate formation. The most effective resulted in an 86% reduction in bromate formation. At typical plant conditions, this represents a near zero risk of ever exceeding the MCL for bromate. Overall, having ammonia in excess causes an improvement in bromate prevention throughout all conditions, with the exception of the final condition. The best bromate formation reduction occurred in the 0.75 mg/L Cl_2 conditions, with a similar ratio to the successful conditions at 0.25 mg/L and 0.5 mg/L Cl_2. It is important to note the similarity between the results presented in this study and the results presented by Wert et al. (2007) despite the significant difference in water quality parameters. The Wert study utilized Lake Mead water with the following characteristics: Alkalinity (137 mg/L), total hardness (288 mg/L $CaCO_3$), TOC (2.59 mg/L), and pH

(7.95). The optimal ratio found with Lake Mead water was 0.5 mg/L NH_3 to 0.5 mg/L Cl_2, which was the highest concentration investigated by Wert et al. (2007). This ratio produced less than 1 ppb bromate at a CT of 4.41 min·mg/L, compared to 0.3 mg/L NH_3 to 0.5 mg/L Cl_2 which produced 3.3 ppb bromate at a CT of 3.9 min·mg/L. For comparison, in this study the best ratio is 0.45 mg/L NH_3 to 0.75 mg/L Cl_2 which produced 1.09 ppb bromate at a CT of 6.8 min*mg/L. While further research is needed, this appears to illustrate the effectiveness 1:1 mass ratio of NH_3:Cl_2 at a concentration of at least 0.5 mg/L Cl_2 across many variations of source water.

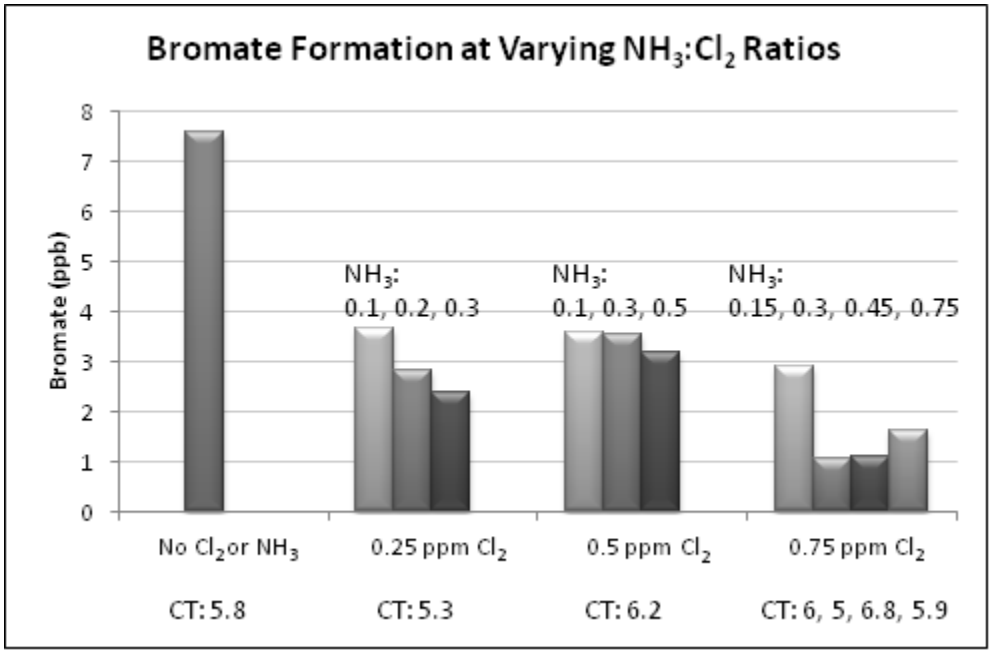


Figure 4.7: Bromate formation at varying NH_3:Cl_2 ratios

4.3.1: Cost Savings

To determine the cost benefits of switching to an increased ozonation pH, the buffer capacity of the water was determined by experiment. Based on this data, an estimation of the increased amount of lime and the decreased amount of caustic soda could be

determined. Lime usage would increase by about 21% of the total required pH increase, and caustic would decrease by 11%.

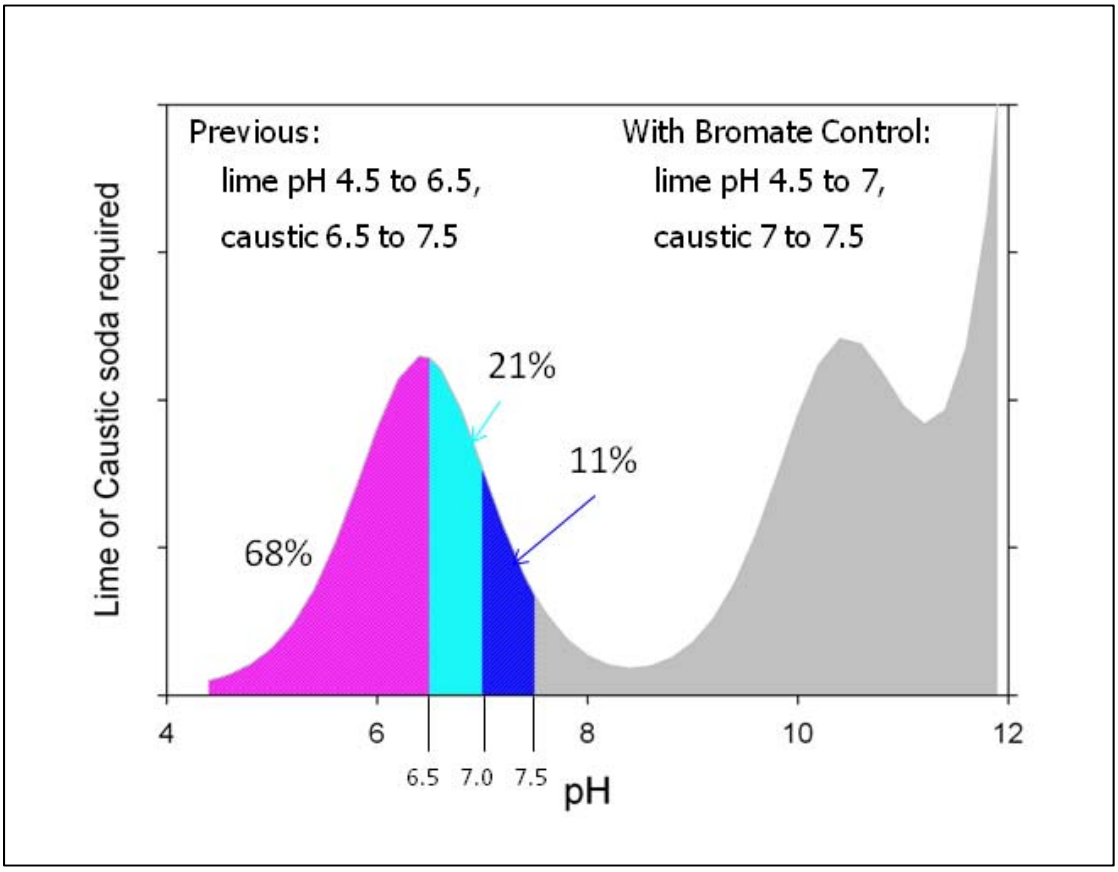
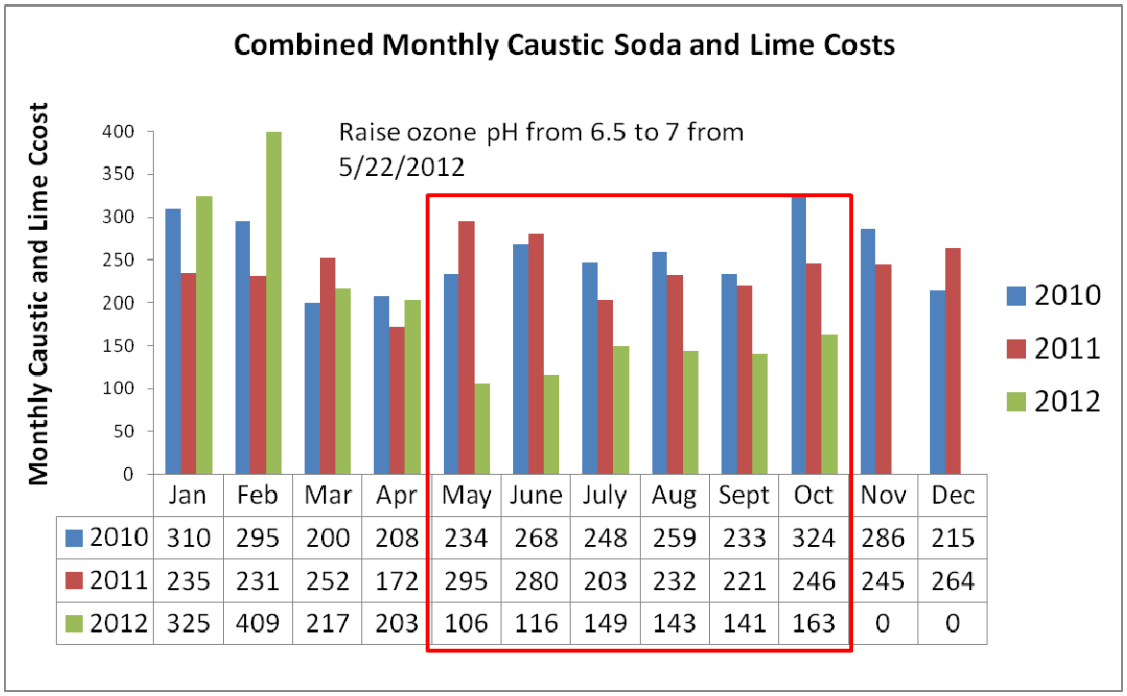


Figure 4.8: Theoretical buffer capacity curve showing percentages of pH change by lime and caustic soda

Because the DLTWTF typically has no bromate concerns outside of the months of January-May, the decision was made to increase the pH prior to completion of the full scale plant's ammonia and chlorine pre-ozonation dosing facilities, which will be installed before the winter of 2013, when bromate will again be an issue. On May 22nd, 2012 the pH of ozonation was increased to 7.0. The change immediately resulted in cost savings in the coming months. To determine the benefit of the change, costs for lime and caustic soda from the previous year were compared to the current year. Because of the

bivalent nature of lime combined with its significantly lower cost over caustic soda, the treatment plant has saved $495,500 compared to the average of 2010 and 2011 since May of 2012. The month by month costs can be seen in Figure 4.10 below. Because caustic and lime are both used in significantly higher quantities during the winter, it is predicted that 2013 savings will be over $1 million.



	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec
2010	310	295	200	208	234	268	248	259	233	324	286	215
2011	235	231	252	172	295	280	203	232	221	246	245	264
2012	325	409	217	203	106	116	149	143	141	163	0	0

Figure 4.9: Combined monthly caustic soda and lime costs at the DLTWTF from 2010-2012.

4.3.2: Conclusion

Bromate control using the chlorine-ammonia process is very effective, resulting in a 50% reduction in bromate over the control group in the worst case and an 86% reduction in the best case. A ratio of around 1:1 NH_3:Cl_2 with a concentration of between 0.4-0.75 mg/L appears to be the most effective for multiple source waters with varying water quality parameters. While the ideal ratio may still vary for untested water quality

matrices, it is likely that many utilities without the resources to perform their own bench or pilot scale tests could utilize this ratio without further testing due to the efficacy of the process compared to the control and the evidence of the effectiveness of this ratio.

Chapter 5: Conclusions and Recommendations for Further Research

In Chapter 1, four major specific objectives were identified. The first two were addressed in chapter 3:

1. Reduce the chlorine demand in filter effluent of the biofiltration system, and,
2. Reduce the operation costs of the biofiltration and/or disinfection system.

To achieve these objectives, two possible causes for non-ideal biofiltration performance were identified. The first is a lack of bioactivity, allowing NOM and other soluble microbial products to pass into the distribution system, increasing chloramine demand and distribution system nitrification. This is a possible scenario as all the biofilters are backwashed with finished water from the clearwells, which have a residual chloramine concentration of about 5 mg/L. A high chloramine concentration may significantly suppress bioactivity in the filter media. The second possible cause is an excess of bioactivity, leading to excessive sloughing of biofilms into the finished water and the same negative effects. Surface water in Florida is high in NOM, which after ozone treatment will be broken down into lower molecular weight NOM that microorganisms can utilize as a source of carbon (a nutrient). Such favorable conditions might cause the filters to become overloaded with biofilm leading to more microbial soluble products in the filter effluent.

Based on these two possible causes, non-chlorinated water for filter backwash and nutrient addition were evaluated, both of which should promote more bioactivity in the filter media. Non-chlorinated water had a profound effect on the chloramine demand of

both GAC and anthracite filters, reducing GAC chloramine demand by approximately 30% and anthracite chloramine demand by approximately 50%. This brought the chloramine demand of each to the level of the filter influent chloramine decay, which is effectively the floor for chloramine demand improvement. Non-chlorinated backwash water had little effect on percent TOC and carboxylic acids removal, with anthracite performing slightly worse than GAC for carboxylic acids removal. Filter run times improved significantly with non-chlorinated backwash. Because a side by side comparison cannot be made, filter run times were compared to the full scale system. At times, the pilot filters had run times over 100% better than the full scale system, averaging approximately 40% longer run times than the full scale system. When GAC effluent under chlorinated backwash water conditions were filtered through a 0.45 μm filter, a 15% decrease in chloramine decay was noted in the filtered water. No variance between the filtered and unfiltered samples was noted with non-chlorinated backwash water. The exact nature of this >0.45 μm material is currently unknown, and future research should focus on determining what these substances are and why they appear during chlorinated backwash water conditions. It is possible that the substances are some sort of soluble microbial products, which are relatively well studied in wastewater treatment but not in drinking water treatment.

Nutrient addition to the tops of filters showed little to no effect for any metric using the limiting nutrient ratio of 100:10:1 of carbon:nitrogen:ammonia, using TOC to determine the additional ammonia and phosphorus required. It is unknown why it did not exhibit the improvements shown in the literature. The theory behind nutrient addition is sound, so future research should focus on measuring nutrients in the effluent to determine if

they are being utilized. Increased dosages should also be attempted to determine if an increased concentration is required to see an effect.

Based on these results, it is likely that bioactivity was being inhibited by chlorinated backwash water. A switch to non-chlorinated backwash water at the full scale plant would result in a cost savings of approximately $300,000 a year, half coming from decreased chlorine and ammonia usage and half from decreased backwash water usage from improved filter performance.

The latter two objectives were addressed in Chapter 4:

3. Reduce bromate formation during ozonation through chemical addition, and,
4. Reduce the operating cost of pH management by increasing ozonation pH without the risk of a bromate violation

A bench scale system was designed and built to evaluate various ratios of chlorine and ammonia to find the ideal concentration and ratio for reducing the formation of bromate at the DLTWTF. Bromate control using the chlorine-ammonia process is very effective, resulting in a 50% reduction in bromate over the control group in the worst case and an 86% reduction in the best case. A ratio of around 1:1 NH_3:Cl_2 with a concentration of between 0.4-0.75 mg/L NH_3-Cl_2 appears to be the most effective for multiple source waters with varying water quality parameters. While the ideal ratio may still vary for untested water quality matrices, it is likely that many utilities without the resources to perform their own bench or pilot scale tests could utilize this ratio without further testing

due to the efficacy of the process compared to the control and the evidence of the effectiveness of this ratio.

The pH of ozonation was already increased at the DLTWTF after the dry season of 2012, giving hard numbers for the savings that can be realized through chlorine-ammonia bromate control. Because bromate can be controlled via the chlorine-ammonia process, the pH of ozonation can be increased from 6.5 to 7, allowing additional lime use and decreased caustic soda use. Between May and August of 2012, the DLTWTF had already saved $495,500 compared to averages for 2010 and 2011 by using increased lime prior to ozonation. It is estimated that a savings of over $1 million can be realized in 2013.

Future research on the chlorine-ammonia process should focus on developing an empirical model of the chlorine-ammonia process to estimate the ideal ratio and concentration given variables such as TOC, pH, alkalinity, bromide, ozone exposure (CT), chlorine, and ammonia. The model should be based on varying source water quality to give it the most breadth. A model such as this would allow utilities like the DLTWTF to avoid the cost of performing bench scale tests to determine the ideal dosage for their location.

To develop a model such as this, a flow through ozone contactor would need to be used, similar to one used in full scale water treatment. CT could be controlled extremely well using a flow through system, allowing for results that are much more consistent than presented in this study. Then bromide, chlorine, and ammonia concentrations could be varied to provide the data for the model. The other variables would be determined by

the particular source waters used; ideally extremely different waters could be utilized. For example, the well studied Colorado River water and a very humic water such as the Hillsborough River water could be compared. If the same multiple-regression model could be proved accurate to an acceptable degree for multiple source waters, it would give utilities significant confidence in the ability of the tool to predict the ideal ratio for their systems, even with their own varying water quality parameters.

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APPENDICES

Appendix A: Biofiltration

A.1: Raw Biofiltration Data

Table A.1: Full Scale Filtration Data

		Full-Scale			
Date	Analysis (units are the same first set for all sets)	Pre-ozone	Post-ozone	Pre-BAC	Post-BAC
5/2/2011	Acetate (ppb)	87.0	279.5	193.7	37.3
5/2/2011	Acetate as C (ppb)	17.7	56.8	39.4	7.6
5/2/2011	Removal %				**81**
5/2/2011	Formate (ppb)	74.9	281.2	237.4	51.1
5/2/2011	Formate as C (ppb)	20.0	75.0	63.3	13.6
5/2/2011	Removal %				**78**
5/2/2011	Oxalate (ppb)	51.3	699.0	751.7	68.9
5/2/2011	Oxalate as C (ppb)	7.0	95.4	102.6	9.4
5/2/2011	Removal %				**91**
5/2/2011	Total Carboxyl (ppb)	**45**	**227**	**205**	**31**
5/2/2011	Removal %				**85**
5/2/2011	AOC (ppb as C)	**110**	**1000**	**960**	**300**
5/2/2011	Removal %				**69**
5/2/2011	% Carboxyl	**41**	**23**	**21**	**10**
5/2/2011	pH	6.66	6.54	7.71	7.56
5/2/2011	Temperature (°C)	25.4	26.0	27.6	27.4
5/2/2011	TOC (mg/L)	4.5	4.2	4.2	3.2
5/2/2011	Removal %				**24**
5/10/2011	Acetate (ppb)	13.3	109.2	105.2	23.9

Appendix A Continued

Table A.1 (Continued)

5/10/2011	Acetate as C	2.7	22.2	21.4	4.9
5/10/2011	Removal %				**77**
5/10/2011	Formate (ppb)	7.2	107.3	125.1	20.5
5/10/2011	Formate as C	1.9	28.6	33.4	5.5
5/10/2011	Removal %				**84**
5/10/2011	Oxalate (ppb)	7.9	335.5	364.3	39.7
5/10/2011	Oxalate as C	1.1	45.8	49.7	5.4
5/10/2011	Removal %				**89**
5/10/2011	Total Carboxyl	**6**	**97**	**104**	**16**
5/10/2011	Removal %				**85**
5/10/2011	pH				
5/10/2011	Temperature				
5/10/2011	TOC				
6/13/2011	Acetate (ppb)	5.9	78.1	53.3	10.7
6/13/2011	Acetate as C	1.2	15.9	10.8	2.2
6/13/2011	Removal %				**80**
6/13/2011	Formate (ppb)	11.7	108.6	84.6	18.3
6/13/2011	Formate as C	3.1	29.0	22.6	4.9
6/13/2011	Removal %				**78**
6/13/2011	Oxalate (ppb)	3.0	138.0	159.4	18.6
6/13/2011	Oxalate as C	0.4	18.8	21.7	2.5
6/13/2011	Removal %				**88**
6/13/2011	Total Carboxyl	**5**	**64**	**55**	**10**
6/13/2011	Removal %				**83**
6/13/2011	pH	6.36	6.53	7.51	7.38

Appendix A Continued

Table A.1 (Continued)

6/13/2011	Temperature	28.2	28.9	29.5	29.6
6/13/2011	TOC	1.7	1.7	1.7	1.4
6/13/2011	Removal %				**18**
Switched to non-chlorinated water for filter backwash on 06/17/2011.					
7/18/2011	Acetate (ppb)	5.8	99.0	102.5	8.8
7/18/2011	Acetate as C	1.2	20.1	20.8	1.8
7/18/2011	Removal %				**91**
7/18/2011	Formate (ppb)	24.0	129.2	135.1	27.6
7/18/2011	Formate as C	6.4	34.5	36.0	7.4
7/18/2011	Removal %				**80**
7/18/2011	Oxalate (ppb)	7.9	338.2	343.4	23.3
7/18/2011	Oxalate as C	1.1	46.1	46.9	3.2
7/18/2011	Removal %				**93**
7/18/2011	Total Carboxyl	**9**	**101**	**104**	**12**
7/18/2011	Removal %				**88**
7/18/2011	pH	6.69	6.73	7.68	7.49
7/18/2011	Temperature	27.7	28.9	28.5	29
7/18/2011	TOC	2.3	2.2	2.1	1.4
7/18/2011	Removal %				**33**
8/15/2011	Acetate (ppb)	49.4	227.2	231.5	29.9
8/15/2011	Acetate as C	10.1	46.2	47.1	6.1
8/15/2011	Removal %				**87**
8/15/2011	Formate (ppb)	27.1	263.8	262.2	39.4
8/15/2011	Formate as C	7.2	70.4	69.9	10.5
8/15/2011	Removal %				**85**

Appendix A Continued

Table A.1 (Continued)

8/15/2011	Oxalate (ppb)	6.0	298.7	340.8	31.4
8/15/2011	Oxalate as C	0.8	40.8	46.5	4.3
8/15/2011	Removal %				**91**
8/15/2011	Total Carboxyl	**18**	**157**	**164**	**21**
8/15/2011	Removal %				**87**
8/15/2011	pH	5.71	6.04	7.12	7.45
8/15/2011	Temperature	28.22	28.86	28.1	29.78
8/15/2011	TOC	2.8	2.6	2.6	2
8/15/2011	Removal %				**23**
8/15/2011	Acetate (ppb)	144.1	304.2	213.2	127.8
8/15/2011	Acetate as C	29.3	61.9	43.4	26.0
8/15/2011	Removal %				**40**
8/15/2011	Formate (ppb)	66.4	308.5	277.0	78.7
8/15/2011	Formate as C	17.7	82.3	73.9	21.0
8/15/2011	Removal %				**72**
8/15/2011	Oxalate (ppb)	13.9	350.6	373.7	38.7
8/15/2011	Oxalate as C	1.9	47.8	51.0	5.3
8/15/2011	Removal %				**90**
8/15/2011	Total Carboxyl	**49**	**192**	**168**	**52**
8/15/2011	Removal %				**69**
8/15/2011	pH				
8/15/2011	Temperature				
8/15/2011	TOC	2.8	2.6	2.0	2.6
8/15/2011	Removal %				**-30**
9/19/2011	Acetate (ppb)	85.9	237.4	212.5	26.0
9/19/2011	Acetate as C	17.5	48.3	43.2	5.3

Appendix A Continued

Table A.1 (Continued)

9/19/2011	Removal %				**88**
9/19/2011	Formate (ppb)	49.5	309.2	268.0	49.9
9/19/2011	Formate as C	13.2	82.5	71.5	13.3
9/19/2011	Removal %				**81**
9/19/2011	Oxalate (ppb)	8.2	429.7	494.9	44.5
9/19/2011	Oxalate as C	1.1	58.6	67.5	6.1
9/19/2011	Removal %				**91**
9/19/2011	Total Carboxyl	**32**	**189**	**182**	**25**
9/19/2011	Removal %				**86**
9/19/2011	AOC (ppb as C)			**1400**	**340**
9/19/2011	Removal %				**76**
9/19/2011	% Carboxyl			**13**	**7**
9/19/2011	pH	6.24	6.23	7.79	7.55
9/19/2011	Temperature	26.17	27.23	27.17	27.83
9/19/2011	TOC	4.0	3.6	3.6	2.7
9/19/2011	Removal %				**25**
9/19/2011	Acetate (ppb)				
9/19/2011	Acetate as C				
9/19/2011	Removal %				
9/19/2011	Formate (ppb)				
9/19/2011	Formate as C				
9/19/2011	Removal %				
9/19/2011	Oxalate (ppb)				
9/19/2011	Oxalate as C				
9/19/2011	Removal %				
9/19/2011	Total Carboxyl				

Appendix A Continued

Table A.1 (Continued)

9/19/2011	Removal %				#DIV/0!
9/19/2011	AOC (ppb as C)				
9/19/2011	pH				
9/19/2011	Temperature				
9/19/2011	TOC				
	Removal %				#DIV/0!
10/24/2011	Acetate (ppb)			151.8	31.4
10/24/2011	Acetate as C			30.9	6.4
10/24/2011	Removal %				79
10/24/2011	Formate (ppb)			216.2	43.4
10/24/2011	Formate as C			57.7	11.6
10/24/2011	Removal %				80
10/24/2011	Oxalate (ppb)			327.9	49.6
10/24/2011	Oxalate as C			44.7	6.8
10/24/2011	Removal %				85
10/24/2011	Total Carboxyl			133	25
10/24/2011	Removal %				81
10/24/2011	pH			7.85	7.77
10/24/2011	Temperature			20.88	21.25
10/24/2011	TOC			3.5	2.8
	Removal %				20
11/14/2011	Acetate (ppb)	15.0	111.6	126.9	30.9
11/14/2011	Acetate as C	3.1	22.7	25.8	6.3
11/14/2011	Removal %				76
11/14/2011	Formate (ppb)	13.6	156.4	195.3	39.2
11/14/2011	Formate as C	3.6	41.7	52.1	10.4
11/14/2011	Removal %				80
11/14/2011	Oxalate (ppb)	23.0	258.1	274.8	34.8

Appendix A Continued

Table A.1 (Continued)

11/14/2011	Oxalate as C	3.1	35.2	37.5	4.7
11/14/2011	Removal %				**87**
11/14/2011	Total Carboxyl	**10**	**100**	**115**	**21**
11/14/2011	Removal %				**81**
11/14/2011	pH	6.87	6.7	7.18	7.42
11/14/2011	Temperature	20.19	19.95	21.14	20.15
11/14/2011	TOC	4.1	3.8	3.9	3.3
11/14/2011	Removal %				**15**
12/12/2011	Acetate (ppb)	109.1	191.1	199.4	235.1
12/12/2011	Acetate as C				
12/12/2011	Removal %				
12/12/2011	Formate (ppb)	60.1	177.5	223.3	225.4
12/12/2011	Formate as C				
12/12/2011	Removal %				
12/12/2011	Oxalate (ppb)	12.7	290.9	284.6	53.9
12/12/2011	Oxalate as C				
12/12/2011	Removal %				
12/12/2011	Total Carboxyl				
12/12/2011	Removal %				
12/12/2011	AOC (ppb as C)				
12/12/2011	AOC (ppb as C)				
12/12/2011	pH	6.13	6.16	7.57	7.43
12/12/2011	Temperature	19.85	19.73	20.04	20.59
12/12/2011	TOC	4.3	4.4	4.3	3.7
	Removal %				**14**

Appendix A Continued

Table A.1 (Continued)

12/12/2011					
		Full-Scale			
		Pre-ozone	Post-ozone	Pre-BAC	Post-BAC
12/12/2011	Acetate (ppb)	148.0	201.9	257.5	149.5
	Acetate as C				
(HX6)	Removal %				
	Formate (ppb)	163.7	248.0	338.0	178.9
Traditional	Formate as C				
Sample	Removal %				
Treatment	Oxalate (ppb)	12.9	248.3	279.1	41.4
(On-Guard	Oxalate as C				
Cartridge)	Removal %				
	Total Carboxyl				
	Removal %				
UL lab	AOC (ppb as C)				
MWH lab	AOC (ppb as C)				
	pH	6.13	6.16	7.57	7.43
	Temperature	19.85	19.73	20.04	20.59
	TOC	4.3	4.4	4.3	3.7
	Removal %				**14**
		Full-Scale			
		Pre-ozone	Post-ozone	Pre-BAC	Post-BAC
12/12/2011	Acetate (ppb)	38.0	114.1	135.8	23.8
12/12/2011	Acetate as C	7.7	23.2	27.6	4.8
12/12/2011	Removal %				**82**
12/12/2011	Formate (ppb)	83.9	175.3	229.8	41.1
12/12/2011	Formate as C	22.4	46.8	61.3	11.0
12/12/2011	Removal %				**82**
12/12/2011	Oxalate (ppb)	6.6	254.7	266.1	34.5

Appendix A Continued

Table A.1 (Continued)

12/12/2011	Oxalate as C	0.9	34.8	36.3	4.7
12/12/2011	Removal %				**87**
12/12/2011	Total Carboxyl	**31**	**105**	**125**	**20**
12/12/2011	Removal %				**84**
12/12/2011	AOC (ppb as C)	**42**		**140**	**98**
12/12/2011	AOC (ppb as C)				
12/12/2011					**30**
12/12/2011	pH	6.13	6.16	7.57	7.43
12/12/2011	Temperature	19.9	19.7	20.0	20.6
12/12/2011	TOC	4.3	4.4	4.3	3.7
	Removal %				**14**
1/3/2012	Acetate (ppb)	156.1	196.4		
1/3/2012	Acetate as C	31.8	40.0		
1/3/2012	Removal %				
1/3/2012	Formate (ppb)	222.5	315.9		
1/3/2012	Formate as C	59.4	84.3		
1/3/2012	Removal %				
1/3/2012	Oxalate (ppb)	12.7	170.8		
1/3/2012	Oxalate as C	1.7	23.3		
1/3/2012	Removal %				
1/3/2012	Total Carboxyl	**93**	**148**		
1/3/2012	Removal %				
4/30/2012	Acetate (ppb)	31	99	90	57
4/30/2012	Acetate as C	6.3	20.1	18.3	11.6
4/30/2012	Removal %				**37**
4/30/2012	Formate (ppb)	4.6	77	80	11
4/30/2012	Formate as C	1.2	20.5	21.3	2.9
4/30/2012	Removal %				**86**

Appendix A Continued

Table A.1 (Continued)

4/30/2012	Oxalate (ppb)	0	72	77	13
4/30/2012	Oxalate as C	0.0	10	10.5	1.8
4/30/2012	Removal %				83
4/30/2012	Total Carboxyl	8	51	50	16
4/30/2012	Removal %				67
4/30/2012	AOC (ppb as C)	49		160	34
4/30/2012	AOC (ppb as C)				
4/30/2012	Removal %				79
4/30/2012	% Carboxyl	15		31	48
4/30/2012	pH	5.95	6.33	7.14	7.11
4/30/2012	Temperature	24.76	25.85	25.5	26.07
4/30/2012	TOC	1.6	1.6	1.7	1.1
4/30/2012	Removal %				35
6/18/2012	Acetate (ppb)	35	78	86	34
6/18/2012	Acetate as C	7.1	15.9	17.5	6.9
6/18/2012	Removal %				60
6/18/2012	Formate (ppb)	8.9	98	122	19
6/18/2012	Formate as C	2.4	26.1	32.5	5.1
6/18/2012	Removal %				84
6/18/2012	Oxalate (ppb)	4.3	116	123	16
6/18/2012	Oxalate as C	0.6	16	16.8	2.2
6/18/2012	Removal %				87
6/18/2012	Total Carboxyl	10	58	67	14
6/18/2012	Removal %				79
6/18/2012	AOC (ppb as C)	580		732	444

Appendix A Continued

Table A.1 (Continued)

6/18/2012	Removal %				39
6/18/2012	% Carboxyl	1.7		9.1	3.2
6/18/2012	pH	6.00	6.16	7.12	7.08
6/18/2012	Temperature	26.5	28.2	28.0	28.3
6/18/2012	TOC	1.9	1.9	2.2	1.5
6/18/2012	Removal %				32
6/18/2012	Ammonia-N				0.095
6/18/2012	PO4-P				
8/6/2012	Acetate (ppb)	32	116	215	47
8/6/2012	Acetate as C	6.5	23.6	43.7	9.6
8/6/2012	Removal %				78
8/6/2012	Formate (ppb)	19	200	270	48
8/6/2012	Formate as C	5.1	53.4	72.0	12.8
8/6/2012	Removal %				82
8/6/2012	Oxalate (ppb)	11	365	465	40
8/6/2012	Oxalate as C	1.5	50	63.4	5.5
8/6/2012	Removal %				91
8/6/2012	Total Carboxyl	13	127	179	28
8/6/2012	Removal %				84
8/6/2012	AOC (ppb as C)	390		1300	380
8/6/2012	Removal %				71
8/6/2012	% Carboxyl	3.4		13.8	7.3
8/6/2012	pH				7.64
8/6/2012	Temperature				24.9
8/6/2012	TOC	5.8	5.6	5.6	4.7

Appendix A Continued

Table A.1 (Continued)

8/6/2012	Removal %				**16**
8/6/2012	Ammonia-N				0.13
8/6/2012	PO4-P				

Table A.2: Pilot filtration data

Date	Analysis (all units same as first set for same analysis)	Pilot BAC #1		Pilot BAC #2		Pilot BAC #3		Pilot BAC #4		Pilot BAC #5		Pilot BAC #6	
		Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
5/2/2011	Acetate (ppb)	78.0	131.0	97.2	19.6	169.3	21.5	97.1	19.1	96.3	105.2	174.3	54.4
5/2/2011	Acetate as C (ppb)	15.9	26.7	19.8	4.0	34.4	4.4	19.8	3.9	19.6	21.4	35.5	11.1
5/2/2011	Removal %		**-68**		**80**		**87**		**80**		**-9**		**69**
5/2/2011	Formate (ppb)	138.4	109.6	145.7	29.2	207.0	36.3	147.3	31.5	147.3	88.2	186.5	52.4
5/2/2011	Formate as C (ppb)	36.9	29.2	38.9	7.8	55.2	9.7	39.3	8.4	39.3	23.5	49.8	14.0
5/2/2011	Removal %		**21**		**80**		**82**		**79**		**40**		**72**
5/2/2011	Oxalate (ppb)	511.7	64.8	538.1	25.9	529.2	39.8	545.1	39.2	545.9	50.3	554.4	47.7
5/2/2011	Oxalate as C (ppb)	69.8	8.8	73.4	3.5	72.2	5.4	74.4	5.3	74.5	6.9	75.7	6.5
5/2/2011	Removal %		**87**		**95**		**92**		**93**		**91**		**91**
5/2/2011	Total Carboxyl(ppb)	**123**	**65**	**132**	**15**	**162**	**19**	**133**	**18**	**133**	**52**	**161**	**32**
5/2/2011	Removal %		**47**		**88**		**88**		**87**		**61**		**80**
5/2/2011	AOC (ppb as C)		**410**				**400**		**340**				**380**
5/2/2011	Removal %		**23**				**25**		**36**				**28**
5/2/2011	% Carboxyl		**16**				**5**		**5**				**8**

Appendix A Continued

Table A.2 (Continued)

5/2/2011	pH	7.71	7.67	7.78	7.40	7.97	7.59	7.99	7.51	7.83	7.57	7.81	7.61
5/2/2011	Temperature (°C)	26.2	26.4	26.4	26.2	26.3	26.2	26.2	25.9	26.4	26.4	26.4	26.2
5/2/2011	TOC (mg/L)	4.2	3.2	4.0	2.7	3.9	2.8	4.3	2.9	4.0	2.9	4.0	3.2
5/2/2011	Removal %		24		33		28		33		28		20
6/13/2011	Acetate (ppb)	72.6	8.4	37.1	7.4	36.8	8.9	38.4	6.3	39.5	10.5	37.8	12.2
6/13/2011	Acetate as C	14.8	1.7	7.5	1.5	7.5	1.8	7.8	1.3	8.0	2.1	7.7	2.5
6/13/2011	Removal		88		80		76		84		73		68
6/13/2011	Formate (ppb)	81.9	14.2	65.5	14.8	65.0	14.8	67.5	13.6	69.3	15.6	68.3	14.6
6/13/2011	Formate as C	21.9	3.8	17.5	3.9	17.3	4.0	18.0	3.6	18.5	4.2	18.2	3.9
6/13/2011	Removal %		83		77		77		80		77		79
6/13/2011	Oxalate (ppb)	112.4	9.1	116.6	13.6	118.4	15.3	109.2	8.4	118.4	12.4	118.3	18.7
6/13/2011	Oxalate as C	15.3	1.2	15.9	1.9	16.2	2.1	14.9	1.1	16.2	1.7	16.1	2.5
6/13/2011	Removal %		92		88		87		92		90		84
6/13/2011	Total Carboxyl	52	7	41	7	41	8	41	6	43	8	42	9
6/13/2011	Removal %		87		82		81		85		81		79
6/13/2011	pH	7.45	7.48	7.48	7.45	7.51	7.49	7.52	7.42	7.54	7.46	7.48	7.49
6/13/2011	Temperature	28.7	29.1	29.3	29.2	29.4	29.3	29.2	29.4	29.3	29.2	29.3	29.1
6/13/2011	TOC	1.8	1.2	1.6	1.1	1.7	1.1	1.7	1.1	1.9	1.2	1.9	1.3
6/13/2011	Removal %		33		31		35		35		37		32
7/18/2011	Acetate (ppb)	36.9	27.1	40.3	2.4	44.7	5.5	40.7	4.1	59.8	9.7	40.2	6.6
7/18/2011	Acetate as C	7.5	5.5	8.2	0.5	9.1	1.1	8.3	0.8	12.2	2.0	8.2	1.3
7/18/2011	Removal %		26		94		88		90		84		84

Appendix A Continued

Table A.2 (Continued)

7/18/2011	Formate)	76.6	32.3	78.0	17.4	80.5	18.3	71.7	19.7	88.0	20.6	77.7	21.1
7/18/2011	Formate as C	20.4	8.6	20.8	4.6	21.5	4.9	19.1	5.2	23.5	5.5	20.7	5.6
7/18/2011	Removal %		58		78		77		73		77		73
7/18/2011	Oxalate (ppb)	181.0	16.5	188.8	13.3	193.4	19.1	195.7	18.9	194.4	18.7	191.3	18.7
7/18/2011	Oxalate as C	24.7	2.3	25.8	1.8	26.4	2.6	26.7	2.6	26.5	2.6	26.1	2.5
7/18/2011	Removal %		91		93		90		90		90		90
7/18/2011	Total Carboxyl	53	16	55	7	57	9	54	9	62	10	55	10
7/18/2011	Removal %		69		87		85		84		84		83
7/18/2011	pH	7.26	7.38	7.44	7.38	7.51	7.46	7.57	7.48	7.62	7.53	7.61	7.61
7/18/2011	Temperature	29.2	29.2	29.3	29.2	29.4	29.2	29.3	28.9	29.3	29.2	29.3	29
7/18/2011	TOC	2.2	1.4	2.0	1.1	2	1.2	2.4	1.3	2.1	1.2	2.2	1.4
7/18/2011	Removal %		36		45		40		46		43		36
8/15/2011	Acetate (ppb)	94.9	119.7	94.9	99.5	88.8	64.5	91.1	95.4	103.2	54.6	102.6	81.9
8/15/2011	Acetate as C	19.3	24.3	19.3	20.2	18.1	13.1	18.5	19.4	21.0	11.1	20.9	16.7
8/15/2011	Removal		-26		-5		27		-5		47		20
8/15/2011	Formate (ppb)	147.6	91.1	147.6	72.4	146.7	41.2	147.6	57.4	155.9	33.9	153.6	48.2
8/15/2011	Formate as C	39.4	24.3	39.4	19.3	39.1	11.0	39.4	15.3	41.6	9.1	41.0	12.9
8/15/2011	Removal %		38		51		72		61		78		69
8/15/2011	Oxalate (ppb)	198.1	21.4	198.1	13.8	197.9	17.3	201.7	16.2	210.8	17.0	209.0	19.4
8/15/2011	Oxalate as C	27.0	2.9	27.0	1.9	27.0	2.4	27.5	2.2	28.8	2.3	28.5	2.6
8/15/2011	Removal %		89		93		91		92		92		91
8/15/2011	Total Carboxyl	86	52	86	41	84	26	85	37	91	22	90	32

Appendix A Continued

Table A.2 (Continued)

8/15/2011	Removal %		40		52		69		57		75		64
8/15/2011	pH	6.45	6.78	7.02	6.99	7.09	7.1	7.22	7.21	7.33	7.36	7.42	7.43
8/15/2011	Temp	29.04	28.96	29.11	29.15	29.12	29	29.07	29.09	29.1	29.03	29.15	29.14
8/15/2011	TOC	2.7	2.6	2.6	1.6	2.6	1.8	2.6	1.8	2.6	1.8	2.7	2.0
8/15/2011	Remove %		4		38		31		31		31		26
8/15/2011	Acetate (ppb)	110.8	116.5	112.9	15.0	105.8	15.9	117.5	26.7	210.5	27.7	122.0	28.6
8/15/2011	Acetate as C	22.5	23.7	23.0	3.1	21.5	3.2	23.9	5.4	42.8	5.6	24.8	5.8
8/15/2011	Removal %		-5		87		85		77		87		77
8/15/2011	Formate (ppb)	167.4	63.7	173.1	25.4	171.6	25.7	171.8	27.2	215.8	28.3	176.7	31.7
8/15/2011	Formate as C	44.7	17.0	46.2	6.8	45.8	6.9	45.8	7.3	57.6	7.5	47.1	8.4
8/15/2011	Removal %		62		85		85		84		87		82
8/15/2011	Oxalate (ppb)	237.6	28.7	230.1	21.9	223.6	31.5	233.9	26.9	242.2	27.6	238.1	32.2
8/15/2011	Oxalate as C	32.4	3.9	31.4	3.0	30.5	4.3	31.9	3.7	33.0	3.8	32.5	4.4
8/15/2011	Removal %		88		90		86		89		89		86
8/15/2011	Total Carboxyl	100	45	101	13	98	14	102	16	133	17	104	19
8/15/2011	Removal %		55		87		85		84		87		82
8/15/2011	pH												
8/15/2011	Temperature												
8/15/2011	TOC	2.7	2.6	2.6	1.6	2.6	1.8	2.6	1.8	2.6	1.8	2.7	2.0
8/15/2011	Removal %		4		38		31		31		31		26
9/19/2011	Acetate (ppb)	108.3	98.4	112.0	20.2	110.8	17.8	119.8	137.0	116.4	22.0	115.4	26.8
9/19/2011	Acetate as C	22.0	20.0	22.8	4.1	22.5	3.6	24.4	27.9	23.7	4.5	23.5	5.5

Appendix A Continued

Table A.2 (Continued)

9/19/2011	Removal %		9		82		84		-14		81		77
9/19/2011	Formate (ppb)	167.6	60.6	173.7	31.2	168.5	33.5	177.3	80.6	179.1	36.9	179.0	39.9
9/19/2011	Formate as C	44.7	16.2	46.3	8.3	44.9	8.9	47.3	21.5	47.8	9.8	47.8	10.6
9/19/2011	Removal %		64		82		80		55		79		78
9/19/2011	Oxalate (ppb)	304.3	30.1	313.7	22.4	312.7	34.6	321.4	25.1	321.3	32.7	324.3	39.4
9/19/2011	Oxalate as C	41.5	4.1	42.8	3.1	42.7	4.7	43.9	3.4	43.8	4.5	44.2	5.4
9/19/2011	Removal %		90		93		89		92		90		88
9/19/2011	Total Carboxyl	108	40	112	16	110	17	116	53	115	19	115	21
9/19/2011	Removal %		63		86		84		54		84		81
9/19/2011	AOC (ppb as C)		760				310		330				450
9/19/2011	Removal %		-19				52		48				30
9/19/2011	% Carboxyl		5				6		16				5
9/19/2011	pH	6.49	6.84	7.05	7.02	7.2	7.21	7.31	7.32	7.45	7.41	7.62	7.95
9/19/2011	Temperatu re	27.52	27.02	27.58	27.51	27.51	27.53	27.46	27.62	27.61	27.37	27.64	27.35
9/19/2011	TOC	3.4	2.8	3.5	2.3	3.4	2.4	3.4	2.4	3.4	2.4	3.5	2.6
9/19/2011	Removal %		18		34		29		29		29		26
9/19/2011	Acetate (ppb)	97.8	33.3					125.1	111.7				
9/19/2011	Acetate as C	19.9	6.8					25.4	22.7				
9/19/2011	Removal %		66						11				
9/19/2011	Formate (ppb)	192.8	45.8					189.8	73.7				
9/19/2011	Formate as C	51.4	12.2					50.6	19.7				
9/19/2011	Removal %		76						61				

Appendix A Continued

Table A.2 (Continued)

9/19/2011	Oxalate (ppb)	311.1	37.8					336.1	27.7				
9/19/2011	Oxalate as C	42.4	5.2					45.9	3.8				
9/19/2011	Removal %		**88**						**92**				
9/19/2011	Total Carboxyl	**114**	**24**					**122**	**46**				
9/19/2011	Removal %		**79**		**#DIV/0!**		**#DIV/0!**		**62**		**#DIV/0!**		**#DIV/0!**
9/19/2011	AOC (ppb as C)		**760**						**330**				
9/19/2011	pH	6.49	6.84					7.31	7.32				
9/19/2011	Temperature	27.52	27.02					27.46	27.62				
9/19/2011	TOC	3.4	2.8					3.4	2.4				
	Removal %		**18**		**#DIV/0!**		**#DIV/0!**		**29**		**#DIV/0!**		**#DIV/0!**
10/24/2011	Acetate (ppb)					161.5	31.1	99.2	31.0			103.4	37.2
10/24/2011	Acetate as C					32.9	6.3	20.2	6.3			21.0	7.6
10/24/2011	Removal %						**81**		**69**				**64**
10/24/2011	Formate (ppb)					212.3	42.2	161.6	34.4			163.6	39.4
10/24/2011	Formate as C					56.6	11.2	43.1	9.2			43.7	10.5
10/24/2011	Removal %						**80**		**79**				**76**
10/24/2011	Oxalate (ppb)					251.5	39.7	246.0	41.2			255.3	43.5
10/24/2011	Oxalate as C					34.3	5.4	33.6	5.6			34.8	5.9
10/24/2011	Removal %						**84**		**83**				**83**
10/24/2011	Total Carboxyl					**124**	**23**	**97**	**21**			**100**	**24**
10/24/2011	Removal %						**81**		**78**				**76**
10/24/2011	pH					7.4	7.44	7.94	7.87			7.94	8.04

Appendix A Continued

Table A.2 (Continued)

10/24/2011	Temperature					21.08	21.6	21.67	21.65			21.68	21.63
10/24/2011	TOC					3.6	2.8	3.5	2.9			3.6	3
	Removal %		#DIV/0!		#DIV/0!		22		17		#DIV/0!		17
11/14/2011	Acetate (ppb)	70.5	31.6			79.7	18.3	87.7	22.9			91.2	23.5
11/14/2011	Acetate as C	14.3	6.4			16.2	3.7	17.8	4.6			18.6	4.8
11/14/2011	Removal %		55				77		74				74
11/14/2011	Formate (ppb)	126.2	55.5			118.9	25.3	132.8	26.1			124.8	31.1
11/14/2011	Formate as C	33.7	14.8			31.7	6.8	35.4	7.0			33.3	8.3
11/14/2011	Removal %		56				79		80				75
11/14/2011	Oxalate (ppb)	203.0	56.2			195.2	36.4	195.2	24.4			193.9	30.1
11/14/2011	Oxalate as C	27.7	7.7			26.6	5.0	26.6	3.3			26.5	4.1
11/14/2011	Removal %		72				81		88				85
11/14/2011	Total Carboxyl	76	29			75	15	80	15			78	17
11/14/2011	Removal %		62				79		81				78
11/14/2011	pH	7.69	7.68			7.67	7.66	7.67	7.69			7.68	7.53
11/14/2011	Temperature	20.05	20.18			20.72	20.11	20.7	20.2			20.18	20.43
11/14/2011	TOC	3.8	3.6			3.9	3.1	3.9	3.1			3.9	3.4
11/14/2011	Removal %		5		#DIV/0!		21		21		#DIV/0!		13
12/12/2011	Acetate (ppb)	169.4	220.9			158.8	93.5	151.6	113.2	126.7		125.0	86.3
12/12/2011	Acetate as C												
12/12/2011	Removal %												

Appendix A Continued

Table A.2 (Continued)

12/12/2011	Formate (ppb)	163.6	222.4			169.4	61.8	157.8	65.3	41.7		143.7	52.2
12/12/2011	Formate as C												
12/12/2011	Removal %												
12/12/2011	Oxalate (ppb)	235.1	69.4			251.6	41.6	226.9	39.5	20.4		232.4	45.7
12/12/2011	Oxalate as C												
12/12/2011	Removal %												
12/12/2011	Total Carboxyl												
12/12/2011	Removal %												
12/12/2011	AOC (ppb as C)												
12/12/2011	AOC (ppb as C)												
12/12/2011	pH	7.6	7.64			7	7.29	6.97	7.24	6.97	7.24	6.66	7.14
12/12/2011	Temperature	20.08	20.54			20.12	20.13	20.29	20.06	20.29	20.06	20.14	20.19
12/12/2011	TOC	4.3	4.0			4.2	3.7	4.2	3.7			4.3	3.7
	Removal %		**7**		**#DIV/0!**		**12**		**12**		**#DIV/0!**		**14**
12/12/2011									filtered 3.7				
		Pilot BAC #1				Pilot BAC #3		Pilot BAC #4		Pilot BAC #4 (0.45 um)		Pilot BAC #6	
		Influent	Effluent			Influent	Effluent	Influent	Effluent		Effluent filtered by 0.45 um	Influent	Effluent
12/12/2011	Acetate (ppb)	82.2	31.6			85.1	19.6	93.3	28.8	104.6		80.5	26.4
	Acetate as C												
(HX6)	Removal %												

Appendix A Continued

Table A.2 (Continued)

	Formate (ppb)	125.6	46.1			127.4	28.2	132.1	37.1	111.6		132.0	38.1
Traditional	Formate as C												
Sample	Removal %												
Treatment	Oxalate (ppb)	196.6	45.5			204.0	29.9	208.3	33.8	16.6		207.5	35.3
(On-Guard	Oxalate as C												
Cartridge)	Removal %												
	Total Carboxyl												
	Removal %												
UL lab	AOC (ppb as C)												
MWH lab	AOC (ppb as C)												
	pH	7.6	7.64			7	7.29	6.97	7.24	6.97	7.24	6.66	7.14
	Temperature	20.08	20.54			20.12	20.13	20.29	20.06	20.29	20.06	20.14	20.19
	TOC	4.3	4.0			4.2	3.7	4.2	3.7			4.3	3.7
	Removal %		**7**		**#DIV/0!**		**12**		**12**		**#DIV/0!**		**14**
		Pilot BAC #1				Pilot BAC #3		Pilot BAC #4		Pilot BAC #4 (0.45 um)		Pilot BAC #6	
		Influent	Effluent			Influent	Effluent	Influent	Effluent		Effluent filtered by 0.45	Influent	Effluent
12/12/2011	Acetate (ppb)	93.7	28.6			103.4	20.0	140.2	21.9	20.8		104.2	22.9
12/12/2011	Acetate as C	19.1	5.8			21.0	4.1	28.5	4.5	4.2		21.2	4.7
12/12/2011	Removal %												
12/12/2011	Formate (ppb)	206.4	44.3			184.1	30.1	281.4	32.6	21.3		193.7	33.9

Appendix A Continued

Table A.2 (Continued)

12/12/2011	Formate as C	55.1	11.8			49.1	8.0	75.1	8.7	5.7		51.7	9.0
12/12/2011	Removal %												
12/12/2011	Oxalate (ppb)	199.4	47.9			208.6	28.6	207.1	30.0	15.3		207.3	35.9
12/12/2011	Oxalate as C	27.2	6.5			28.5	3.9	28.3	4.1	2.1		28.3	4.9
12/12/2011	Removal %												
12/12/2011	Total Carboxyl	**101**	**24**			**99**	**16**	**132**	**17**	**12**		**101**	**19**
12/12/2011	Removal %		**76**				**84**		**87**				**82**
12/12/2011	AOC (ppb as C)		**61**				**56**		**54**				**68**
12/12/2011	AOC (ppb as C)												
12/12/2011			**59**				**63**		**64**				**55**
12/12/2011	pH	7.60	7.64			7.00	7.29	6.97	7.24	6.97	7.24	6.66	7.14
12/12/2011	Temperature	20.1	20.5			20.1	20.1	20.3	20.1	20.3	20.1	20.1	20.2
12/12/2011	TOC	4.3	4.0			4.2	3.7	4.2	3.7			4.3	3.7
	Removal %		**7**		**#DIV/0!**		**12**		**12**		**#DIV/0!**		**14**
1/3/2012	Acetate (ppb)	152.6	Re-analysis for 12-12-2011					152.1	Re-analysis for 12-12-2011				
1/3/2012	Acetate as C	31.0						30.9					
1/3/2012	Removal %												
1/3/2012	Formate (ppb)	225.6						213.4					
	Formate as C	60.2						56.9					

Appendix A Continued

Table A.2 (Continued)

	Removal %												
1/3/2012	Oxalate (ppb)	214.4						210.9					
1/3/2012	Oxalate as C	29.3						28.8					
1/3/2012	Removal %												
1/3/2012	Total Carboxyl	120						117					
1/3/2012	Removal %		79.9						85.2				
4/30/2012	Acetate (ppb)	49	28		23	52	33.0	77	30	58	51	61	49.0
4/30/2012	Acetate as C	10.0	5.7		4.7	10.6	6.7	15.7	6.1	11.8	10.4	12.4	10.0
4/30/2012	Removal %		43		#DIV/0!		37		61		12		20
4/30/2012	Formate (ppb)	53	11		6.4	51	9.9	51	7.2	52	8.7	51	9.7
4/30/2012	Formate as C	14.1	2.9		1.7	13.6	2.6	13.6	1.9	13.9	2.3	13.6	2.6
4/30/2012	Removal %		79		#DIV/0!		81		86		83		81
4/30/2012	Oxalate (ppb)	52	14		9.9	54	8.1	62	16.1	79	0.0	56	0.0
4/30/2012	Oxalate as C	7.1	1.9		1.4	7.4	1.1	8.5	2.2	10.8	0.0	7.6	0.0
4/30/2012	Removal %		73		#DIV/0!		85		74		100		100
4/30/2012	Total Carboxyl	31	11		8	32	10	38	10	36	13	34	13
4/30/2012	Removal %		66		#DIV/0!		67		73		65		63
4/30/2012	AOC		48				45		33				35
4/30/2012	AOC (ppb as C)												
4/30/2012	Removal %		45				49		63				#DIV/0!
4/30/2012	% Carboxyl	35	22			36	23	43	31	41		38	36
4/30/2012	pH	6.73	6.85	6.85	6.88	6.98	6.97	6.98	7	7.02	7.01	7.05	7.01
4/30/2012	Temperature	25.85	25.14	26.2	26.12	26.15	26.05	26.2	26.11	26.25	26.16	26.19	26.1

Appendix A Continued

Table A.2 (Continued)

4/30/2012	TOC	1.7	1.3	1.6	1.0	1.6	1.0	1.6	1.0	1.8	1.0	1.5	1.1
4/30/2012	Removal %		24		38		38		38		44		27
6/18/2012	Acetate (ppb)	53	25	49.0	22	46	23	31	25	56	21	44	23.0
6/18/2012	Acetate as C	10.8	5.1	10.0	4.5	9.4	4.7	6.3	5.1	11.4	4.3	9.0	4.7
6/18/2012	Removal %		53		55		50		19		63		48
6/18/2012	Formate (ppb)	64	15	71.0	13.0	71	13.0	76	18.0	72	15.0	76	18.0
6/18/2012	Formate as C	17.1	4.0	18.9	3.5	18.9	3.5	20.3	4.8	19.2	4.0	20.3	4.8
6/18/2012	Removal %		77		82		82		76		79		76
6/18/2012	Oxalate (ppb)	87	ND	81.0	7.5	91	4.0	94	27.0	87	9.0	88	4.3
6/18/2012	Oxalate as C	11.9	ND	11.1	1.0	12.4	0.5	12.8	3.7	11.9	1.2	12.0	0.6
6/18/2012	Removal %		94		91		96		71		90		95
6/18/2012	Total Carboxyl	40	9	40	9	41	9	39	14	42	10	41	10
6/18/2012	Removal %		87		78		79		66		78		76
6/18/2012	AOC (ppb as C)		560		490		550		470		530		610
6/18/2012	Removal %		38		#DIV/0!		#DIV/0!		#DIV/0!		#DIV/0!		#DIV/0!
6/18/2012	% Carboxyl	4.4	1.6	4.4	1.8	4.5	1.6	4.4	2.9	4.7	1.8	4.6	1.7
6/18/2012	pH	6.53	6.74	6.62	6.66	6.70	6.74	6.80	6.79	6.87	6.81	6.91	6.93
6/18/2012	Temp	27.7	28.3	28.3	28.2	28.8	27.8	28.2	28.6	28.7	28.7	28.8	28.5
6/18/2012	TOC	1.9	1.4	2.0	1.2	2.1	1.3	2.0	1.3	2.3	1.3	2.0	1.4
6/18/2012	Removal %		26		40		38		35		43		30
6/18/2012	Ammonia-N		0.1		0.025		0.12		0.055		0.095		0.095
6/18/2012	PO4-P		< 0.01		< 0.01		<0.01		<0.01		<0.01		<0.01

Appendix A Continued

Table A.2 (Continued)

8/6/2012	Acetate (ppb)	104	52	120	43	122	44	123	49	124	54	118	43
8/6/2012	Acetate as C	21.2	10.6	24.4	8.7	24.8	9.0	25.0	10.0	25.2	11.0	24.0	8.7
8/6/2012	Removal %		50		64		64		60		56		64
8/6/2012	Formate (ppb)	161	43	166	35	168	51	163	37	171	38	172	48
8/6/2012	Formate as C	43.0	11.5	44.3	9.3	44.8	13.6	43.5	9.9	45.6	10.1	45.9	12.8
8/6/2012	Removal %		73		79		70		77		78		72
8/6/2012	Oxalate (ppb)	305	35	320	24	331	34	346	29	332	32	362	41
8/6/2012	Oxalate as C	41.6	4.8	43.7	3.3	45.2	4.6	47.2	4.0	45.3	4.4	49.4	5.6
8/6/2012	Removal %		98		93		90		92		90		89
8/6/2012	Total Carboxyl	106	22	112	21	115	27	116	24	116	25	119	27
8/6/2012	Removal %		95		81		76		79		78		77
8/6/2012	AOC (ppb as C)		420		510		380		490		440		540
8/6/2012	Removal %		45		#DIV/0!		#DIV/0!		#DIV/0!		#DIV/0!		#DIV/0!
8/6/2012	% Carboxyl	11.7	5.2	12.5	4.2	12.8	7.2	12.9	4.9	12.9	5.8	13.3	5.0
8/6/2012	pH		7.67		7.62		7.56		7.53		7.65		7.75
8/6/2012	Temperature		24.8		25.3		25.2		25.2		25.2		24.8
8/6/2012	TOC	5.5	4.6	5.9	4.6	6.5	4.6	7.4	4.6	5.6	4.6	9.7	5.0
8/6/2012	Removal %		16		22		29		38		18		48
8/6/2012	Ammonia-N		0.06		0.065		0.04		0.07		0.07		0.11
8/6/2012	PO4-P		0.0151		<0.01		0.0156		0.0158		<0.01		

Appendix B: Bromate Control

B.1: Dissolved Ozone Calculation

The equation used for calculation of dissolved ozone was derived from Standard Method 4500-Ozone.

The general form of the equation used is:

$$\boldsymbol{C_{liq,O3}} = \frac{\mathbf{2.4}}{\mathbf{b}} * \frac{\mathbf{A_{Indigo} * f - A_{Sample}}}{\mathbf{(1 - f)}} \tag{B.1}$$

Where A_{Indigo} [-] is the absorbance of the blank indigo reagent, A_{sample} is the absorbance of the sample added to an indigo solution, 2.4 is a sensitivity constant calibrated by the change in molar absorbance of indigo per mole of ozone, and f is a dilution factor provided by the following equation:

$$\boldsymbol{f} = \frac{\boldsymbol{V_{Indigo}}}{\boldsymbol{V_{Indigo} + V_{Sample}}} \tag{B.2}$$

The standard method does not use a dilution factor, instead creating a blank with 10ml of indigo reagent and 90ml of distilled water, with the sample having 10ml of indigo reagent and 90ml of sample water. The general form of the standard method equation is:

$$\boldsymbol{C_{liq,O3}} = \frac{\mathbf{2.4}}{\boldsymbol{b}} * \frac{\mathbf{100} * \boldsymbol{\Delta A}}{\boldsymbol{V_{Sample}}} \tag{B.3}$$

Equation B.3 can be expanded to:

$$\boldsymbol{C_{liq,O3}} = \frac{\mathbf{2.4}}{\boldsymbol{b}} * \frac{\mathbf{100} * (\boldsymbol{A_{Blank} - A_{Sample}})}{\boldsymbol{V_{Sample}}} \tag{B.4}$$

The absorbance of the blank can be considered equal to the indigo absorbance in equation B.1 multiplied by the dilution factor.

$$\boldsymbol{A_{Blank} = f * A_{Indigo}} \tag{B.5}$$

Appendix B Continued

Inserting the volumes from the standard method into equation B.2 yields:

$$f = \frac{\mathbf{10ml}}{\mathbf{10ml} + \boldsymbol{V_{Sample}}} = \mathbf{0.1} \tag{B.6}$$

Substituting equations B.5 and B.6 into equation B.1 yields:

$$\boldsymbol{C_{liq,O3}} = \frac{\mathbf{2.4}}{\mathbf{b}} * \frac{(\mathbf{A_{Blank}} - \mathbf{A_{Sample}})}{\left(\mathbf{1} - \frac{\mathbf{10ml}}{\mathbf{10ml} + \boldsymbol{V_{Sample}}}\right)} \tag{B.7}$$

$$\boldsymbol{C_{liq,O3}} = \frac{\mathbf{2.4}}{\mathbf{b}} * \frac{(\mathbf{A_{Blank}} - \mathbf{A_{Sample}})(\mathbf{10} + \mathbf{V_{Sample}})}{\left(\mathbf{1} - \frac{\mathbf{10ml}}{\mathbf{10ml} + \boldsymbol{V_{Sample}}}\right)(\mathbf{10} + \mathbf{V_{Sample}})} \tag{B.8}$$

$$\boldsymbol{C_{liq,O3}} = \frac{\mathbf{2.4}}{\mathbf{b}} * \frac{(\mathbf{A_{Blank}} - \mathbf{A_{Sample}})(\mathbf{10} + \mathbf{V_{Sample}})}{\mathbf{V_{Sample}}} \tag{B.9}$$

Recalling that V_{Sample} in the Standard Method is 90ml:

$$\boldsymbol{C_{liq,O3}} = \frac{\mathbf{2.4}}{\mathbf{b}} * \frac{\mathbf{100} * (\mathbf{A_{Blank}} - \mathbf{A_{Sample}})}{\mathbf{V_{Sample}}} \tag{B.10}$$

Which is identical to equation B.4.

Appendix B Continued
B.2: Raw Ozone Data

Table B.1: Raw Bromate Data

Sample Date	Sample ID	Bromate (ppb)	CT
1/27/2012	7-0-0-200 #1	6.18	3.79
1/27/2012	7-0-0-200 #2	5.23	5.26
2/27/2012	7-0-0-200 #3	4.73	3.48
2/27/2012	7-0-0-200 #4	7.42	6.36
2/27/2012	7-0-0-200 #5	10.54	8.50
2/28/2012	7-0-0-200 #6	8.74	4.50
Adjusted	7-0-0-200 #ADJ	7.58	5.80
2/14/2012	7-0.1-0.25-200 #1	2.29	3.91
2/14/2012	7-0.1-0.25-200 #2	4.51	6.16
Adjusted	7-0.1-0.25-200 #ADJ	3.66	5.30
2/14/2012	7-0.2-0.25-200 #1	2.82	5.31
2/29/2012	7-0.2-0.25-200 #2	2.46	4.85
Adjusted	7-0.2-0.25-200 #ADJ	2.81	5.30
2/15/2012	7-0.3-0.25-200 #1	3.89	8.10
2/16/2012	7-0.3-0.25-200 #2	2.51	5.58
Adjusted	7-0.3-0.25-200 #ADJ	2.36	5.30
2/16/2012	7-0.1-0.5-200 #1	2.67	6.11
2/29/2012	7-0.1-0.5-200 #2	4.96	8.70
3/19/2012	7-0.1-0.5-200 #3	4.97	7.40
4/4/2012	7-0.1-0.5-200 #4	4.56	7.90
4/4/2012	7-0.1-0.5-200 #5	5.61	7.20
Adjusted	7-0.1-0.5-200 #ADJ	3.60	6.20
2/16/2012	7-0.3-0.5-200 #1	2.44	2.33
2/16/2012	7-0.3-0.5-200 #2	2.38	2.86
3/22/2012	7-0.3-0.5-200 #3	2.94	4.85
3/26/2012	7-0.3-0.5-200 #4	3.44	7.77
4/5/2012	7-0.3-0.5-200 #5	4.75	9.60
4/5/2012	7-0.3-0.5-200 #6	4.51	7.60
Adjusted	7-0.3-0.5-200 #ADJ	3.53	6.20
2/16/2012	7-0.5-0.5-200 #1	3.03	4.03
2/17/2012	7-0.5-0.5-200 #2	3.25	7.36
3/26/2012	7-0.5-0.5-200 #3	3.37	4.30
4/5/2012	7-0.5-0.5-200 #7	2.99	5.09
Adjusted	7-0.3-0.5-200 #ADJ	3.18	6.20
2/17/2012	7-0.15-0.75-200 #1	2.18	5.64

Appendix B Continued

Table B.1 Continued

2/17/2012	7-0.15-0.75-200 #2	3.35	6.23
Adjusted	7-0.15-0.75-200 #ADJ	2.90	6.00
2/20/2012	7-0.3-0.75-200 #1	1.05	4.26
2/20/2012	7-0.3-0.75-200 #2	1.06	5.19
Adjusted	7-0.3-0.75-200 #ADJ	1.05	5.00
2/20/2012	7-0.45-0.75-200 #1	0.95	6.66
2/20/2012	7-0.45-0.75-200 #2	1.29	7.02
Adjusted	7-0.45-0.75-200 #ADJ	1.09	6.80
2/20/2012	7-0.6-0.75-200 #1	1.44	5.74
2/20/2012	7-0.6-0.75-200 #2	1.87	6.16
Adjusted	7-0.6-0.75-200 #ADJ	1.60	5.90

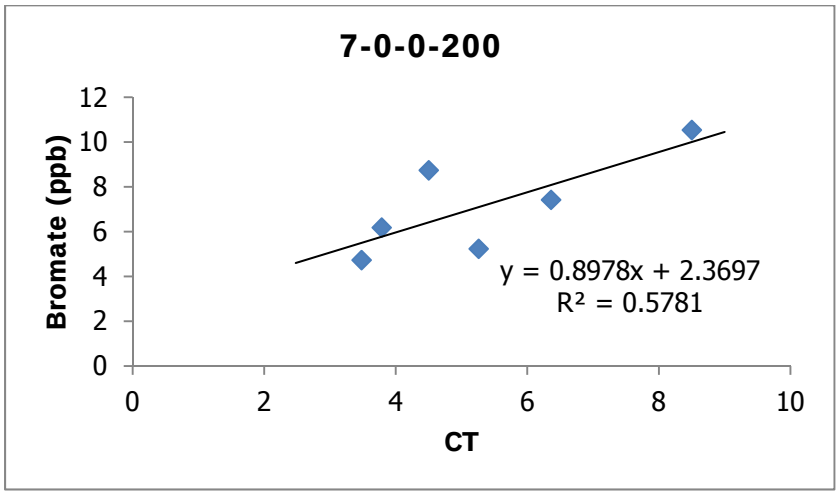

Figure B.1: Regression for condition 7-0-0-200

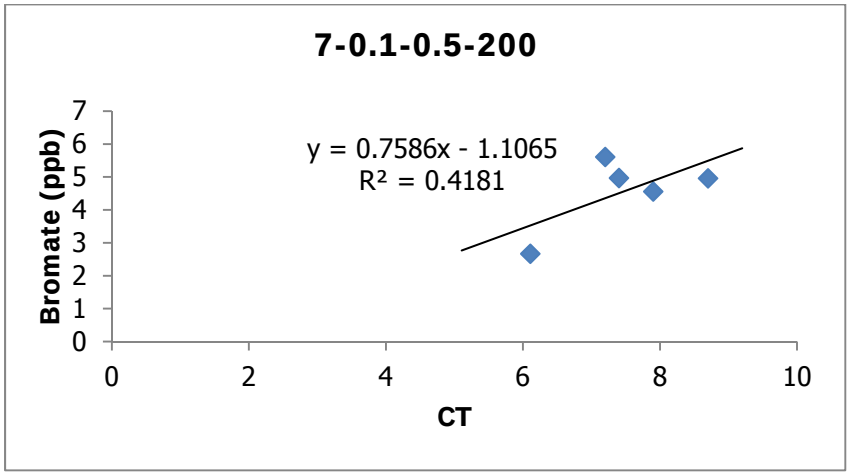

Figure B.2: Regression for condition 7-0.1-0.5-200

Appendix B Continued

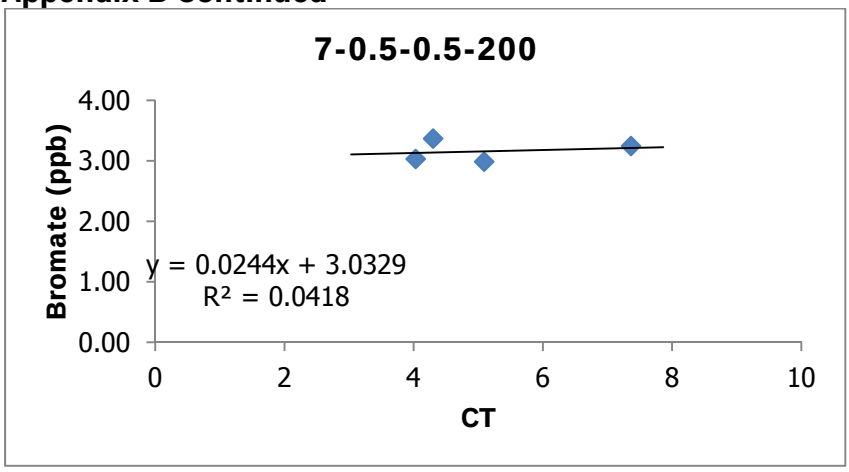

Figure B.3: Regression for condition 7-0.5-0.5-200

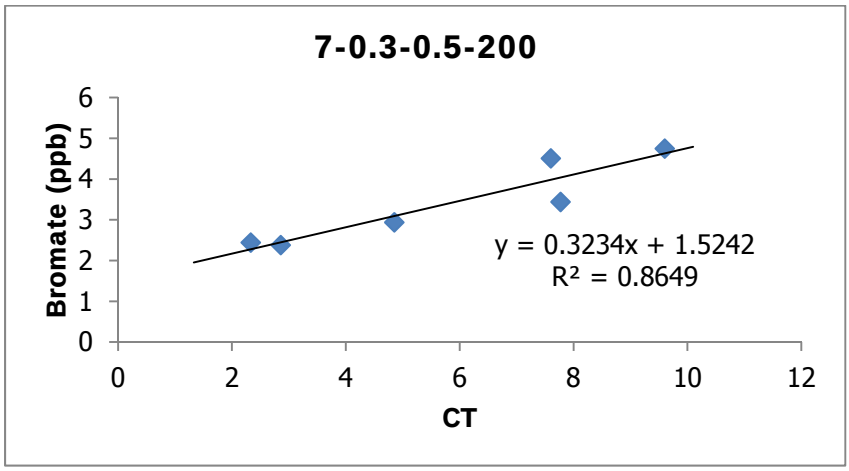

Figure B.4: Regression for condition 7-0.3-0.5-200

Appendix C: Copyright Permission

Figure C.1: Permission for Figure 3.1